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Aquatic Nuisance Species Program

Zebra Mussel Chemical Control Guide

Version 2.0

LeeAnn M. Glomski

July 2015

Environmental Laboratory

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Final report

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Abstract

Zebra mussels were introduced in the mid-1980s to the Great Lakes of North America via ballast water exchange. These highly invasive mollusks have made negative impacts upon native aquatic ecosystems and have been a major concern to managers of all types of water delivery systems, including potable water treatment, agriculture, industry, power generation, and fire protection. Since this invasive organism's introduction, a number of chemicals and biopesticides with previously known or newly discovered molluscicidal properties have been used to control it. The goal of any chemical control program is to choose products that will be effective against the target organism, will work rapidly, and have minimal environmental impact. This report is an update of an original version, *Zebra Mussel Chemical Control Guide*, by S. L. Sprecher and K. D. Getsinger, report number ERDC/EL TR-001, published in January 2000, and describes basic guidelines for the use of those compounds currently registered with the United States Environmental Protection Agency (USEPA) for control of zebra mussels. Included in Version 2.0 is a summary of the USEPA registration process, as well as up-to-date information on available molluscicide products, their use strategies, formulations, mode of action, application rates and techniques, maximum water concentrations, use restrictions, toxicological data, and precautions on product handling.

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Preface

The work reported herein was conducted as part of the Aquatic Nuisance Species Research Program (ANSRP) under the work unit entitled, "Zebra Mussel Chemical Control Guide Update." The ANSRP is sponsored by Headquarters, U.S. Army Corps of Engineers (HQUSACE), and is assigned to the U.S. Army Engineer Research and Development Center (ERDC) under the purview of the Environmental Laboratory (EL), Vicksburg, MS. The HQUSACE Technical Monitor for ANSRP is Joe Wilson.

The purpose of this report is to provide guidance to Corps District and Project personnel on the selection and use of registered chemicals available for control of zebra mussels. The original version of this report, *Zebra Mussel Chemical Control Guide*, by S. L. Sprecher and K. D. Getsinger, report number ERDC/EL TR-001, was published in January 2000. Since that time, other molluscicides and chemical treatment techniques for invasive mollusks have been developed. To update and assist in the treatment selection process, the various types of compounds that were registered as molluscicides at the time that this report was written are summarized with information on use strategies and application rates.

The Principal Investigator for this study was LeeAnn M. Glomski, Environmental Processes Branch (EPP), Environmental Processes and Engineering Division (EP), EL, under the general supervision of Dr. Brandon Lafferty, Chief, EPP; Warren Lorentz, Chief, EP; and Dr. Beth Fleming, Director, EL. Dr. Linda S. Nelson was Program Manager of ANSRP. This report was written by LeeAnn M. Glomski, EPP. Dr. Kurt Getsinger, EPP, contributed information for the section on registration of molluscicides. Technical reviews of this report were provided by Nathan Harms, Aquatic Ecology and Invasive Species Branch (EEA), and Dr. Kurt Getsinger.

At the time of publication of this report, Dr. Jeffery P. Holland was Director of ERDC and LTC John T. Tucker III was Acting Commander of ERDC.

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Abbreviations

ADBAC	Alkyl dimethylbenzyl ammonium chloride
ANSRP	Aquatic Nuisance Species Research Program
cfs	cubic feet per second
CWA	Clean Water Act
DDAC	didecyl dimethyl ammonium chloride
DGH	dodecylguanidine hydrochloride
EC_{50}	effective concentration: concentration causing a 50 percent response in a test system
EEA	Aquatic Ecology and Invasive Species Branch
EL	Environmental Laboratory
EPED	Environmental Processes and Engineering Division
EPP	Environmental Processes Branch
ERDC	Engineer Research and Development Center
EUP	Experimental Use Permit
FAC	free available chlorine
FIFRA	Federal Insecticide Fungicide and Rodenticide Act
HQUSACE	Headquarters United States Army Corps of Engineers
LC_{50}	median lethal concentration: concentration that kills 50 percent of test population

MCL	maximum contaminant level
MRDL	maximum residual disinfectant level
MSDS	Material Safety Data Sheet
NEPA	National Environmental Policy Act
NIOSH	National Institute for Occupational Safety and Health
NOEC	no-effect concentration
NPDES	National Pollutant Discharge Elimination System
Poly-QAC	polyquaternary ammonium compound
ppb	parts per billion
ppm	parts per million
SLN	Special Local Needs
TCC	total combined chlorine
THM	trihalomethanes
TRC	total residual chlorine
U.K.	United Kingdom
U.S.	United States
UV	ultraviolet
USACE	United States Army Corps of Engineers
USBR	United States Bureau of Reclamation
USEPA	United States Environmental Protection Agency

USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
QAC	quaternary ammonium compound
WQBEL	water quality-based effluent limit

Unit Conversion Factors

Multiply	By	To Obtain
acre-feet	1,233.5	cubic meters
cubic feet	0.02831685	cubic meters
gallons (U.S. liquid)	3.785412 E-03	cubic meters
miles (U.S. statute)	1.609344	kilometers
ounces (U.S. fluid)	2.957353 E-05	cubic meters
pounds (mass)	0.45359237	kilograms

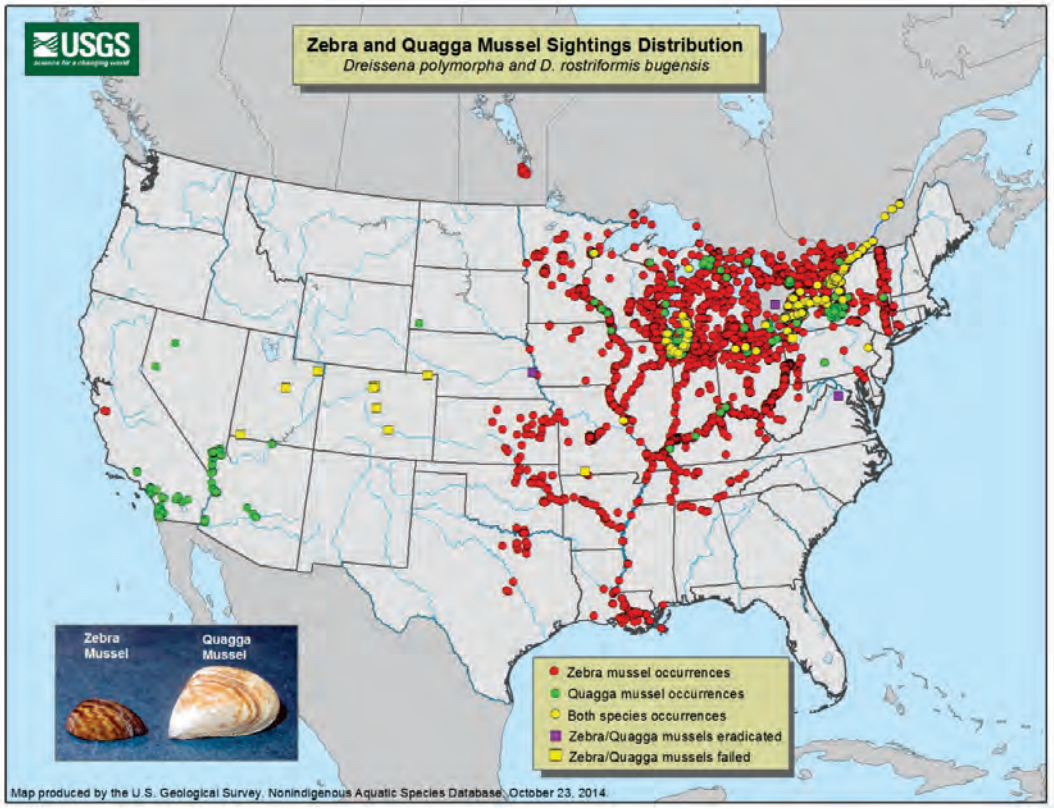
1 Introduction

Background

Native to Eastern Europe (Benson 2014), zebra mussels (*Dreissena polymorpha*) were first reported in North America in the mid-1980s (Hebert et al. 1989). Dreissenids (zebra and quagga mussels) have been documented in 131 river systems and 772 inland reservoirs, lakes, and impoundments in Canada and the United States (Benson 2014), but have continued to spread since the publication of Benson (2014) (Figure 1). Since their introduction, zebra mussels have been a major concern to managers of all types of water delivery systems, including potable water treatment, agriculture, industry, power generation, and fire protection (Mackie and Claudi 2010). Zebra mussels can colonize water intake pipes, reducing water flow and causing severe damage. This can be of particular concern to electric power plants (both fossil fuel driven and nuclear), which rely on a continuous supply of cooling water. Municipal water plants are also impacted by reduction of water flow, but also must deal with decaying flesh that can contaminate the water when zebra mussels die within the pipes (Fisher et al. 1991). Besides restricting water flow, the accumulation of zebra mussels can increase the deterioration of metal and concrete surfaces (Laney 2010).

The U.S. Army Corps of Engineers (USACE) is the largest owner/operator of hydroelectric power plants in the U.S., producing nearly a third of the nation's hydropower (USACE 2009). There are numerous external and internal features of dams and hydroelectric power plants that are vulnerable to problems caused by zebra mussel infestations. These features include: floating structures, gates, weirs, trash racks, sumps, cooling water systems, pumps, turbines, generators, pipes, valves, sensing equipment (level, flow, and pressure) and fire protection (Mackie and Claudi 2010; Prescott et al. 2014). Other USACE facilities that could be impacted by zebra mussel infestations are navigational buoys, docks, boat ramps and swimming areas that have a hard substrate. Because of their sharp edges, mussel shells can be a safety hazard to those walking barefoot; in high densities, zebra mussels have been known to sink navigational buoys (Laney 2010).

Figure 1. Distribution of zebra and quagga mussels in the United States and Canada (USGS 2014).



The U.S. Fish and Wildlife Service (USFWS) estimated the economic impact of zebra mussels to U.S. and Canadian water users in the Great Lakes region to be $5 billion from 2000 to 2010 (USGS 2011). In North America, as in Europe, chemical control has been the most commonly used method for managing zebra mussels in closed, industrial systems (Mackie and Claudi 2010). Numerous organic and inorganic chemicals are toxic to zebra mussels and can be versatile, easy-to-implement, cost-effective methods of dealing with established infestations and can prevent new ones from occurring. While these treatments can be designed to protect whole, closed systems, their major drawback is the requirement for safe discharge into surface waters in compliance with environmental regulations (Mackie and Claudi 2010).

Since the arrival of the zebra mussel, a number of chemicals with previously known or newly discovered molluscicidal properties have been used to control this highly invasive organism. This report describes basic guidelines for the use of those compounds that are currently registered with the United States Environmental Protection Agency (USEPA) for zebra mussel control, including a summary of the important registration process.

Chemical Control of Zebra Mussels

The life cycle and behavior of zebra mussels are important factors to consider when deciding on a chemical control treatment plan. Zebra mussels are well adapted to water temperatures of 12 to 30 °C, pH range of 6.5 to < 9, and turbidity levels common in the Great Lakes and many riverine environments (Farr and Payne 2010). Populations typically start spawning at about 10 to 12 °C, with peak activity occurring at about 17 to 18 °C (Farr and Payne 2010). At the southern end of the zebra mussels' range, it has been documented that veliger density peaks in late May to early June, and then again in September and October when water temperatures fall to 16 to 26 °C. The secondary peak of veliger densities is usually smaller than the spring peak (Boeckman and Bidwell 2014). Females release >40,000 eggs in a reproductive cycle and up to one million per spawning season (Benson et al. 2014). The maximum growth rate for a zebra mussel is 1.5 to 2.0 cm per year and adults are sexually mature within one year (Benson et al. 2014). Densities can reach >200,000 per square meter (Farr and Payne 2010), and individual life spans are 3 to 9 years (Benson et al. 2014). Zebra mussels are filter feeders and can filter about 1 liter of water per day (Benson et al. 2014). When their sensitive chemoreceptors alert them to certain toxins in the environment, they have the ability to close their shells and thereby remain immune to certain biocide contact (Van Benschoten et al. 1993a). Not all molluscicides evoke this response.

The application of molluscicides is limited by several considerations. First, a method must be judged by how well it removes or kills the various life stages of the zebra mussel. Second, any chemical control method used must not be harmful to natural fisheries and aquatic ecosystems, and in certain situations must be compatible with potable water uses. Thus, flow-through systems may require a different suite of chemicals than is possible in static or closed systems where there is no release into the environment. Finally, use of the molluscicide must be cost-effective.

Chemicals identified for zebra mussel control have been derived mainly from water treatment compounds and antifouling biocides and biodispersants. Chlorine has been used for nearly a hundred years in drinking water disinfection, where its properties and behavior in effluent are well known, and it has been the primary chemical for zebra mussel control in Europe. In contrast, molluscicidal properties have been associated only recently with *Pseudomonas fluorescens*, a common bacterium found in North American waterbodies. Investigation of toxicity to

both the target and nontarget organisms in the aquatic environment is the first step in the ongoing effort to identify compounds that will be effective against zebra mussels. While oxidizers, and particularly the various forms of chlorine, continue to be the most commonly used of the chemical controls, additional compounds have been registered (i.e., Natrix™, Zequanox®). The goal of any chemical control program is to choose chemicals that will be effective, work rapidly, and have a minimal environmental impact.

The Use Guide Outline

In the following chapters of this guide, each molluscicide compound is described using the topics in the format described below. The topics are introduced with general information and definitions when assessing the guidelines for individual compounds. Many of these concepts are further defined and discussed by Claudi and Mackie (1994).

The source of information on individual compounds has been primarily the product label and its Material Safety and Data Sheet (MSDS). Both of these documents are available from the manufacturer or vendor and are required by law to be in the possession of the user at the time of molluscicide use.

Chemical Name and Formulations

This topic gives the compound name, brand name of proprietary or commercial formulation, and manufacturer or supplier. If the compound is generic (i.e., chlorine), no supplier is given.

Mode of Action

This topic describes the way in which the compound acts against mussels to produce a toxic or inhibitory effect.

Application Strategies

Application of chemicals to systems and sites usually requires specific chemical feed equipment, piping for chemical transport, diffusers to introduce chemical to the water, and areas for chemical storage or generation (Lawrence 1997). A variety of treatment strategies can be used. Mackie and Claudi (2010) summarize them as *preventative* and *reactive* strategies:

- Preventative strategies are designed to prevent settlement of zebra mussels.

    - Intermittent: This treatment strategy targets postveligers that have recently settled. Postveligers are more susceptible than adults and therefore require lower concentration of chemical and a shorter duration of application. Chemical is applied at frequent intervals (every 12 to 24 hours). This strategy will not kill adults already in the system or those that gain access.
    - Semicontinuous: Zebra mussels close their shells and stop filtering when exposed to noxious substances (oxidizing chemicals). After 15 to 30 minutes, zebra mussels will reopen their shells and start filtering. The semicontinuous treatment takes into account this zebra mussel behavior and adjusts the treatment schedule to 15 minutes on and 15 to 45 minutes off. According to Evans and Sim (1993), this treatment strategy uses significantly less chemical than a continuous treatment while still providing complete control of zebra mussels at all growth stages.
    - Continuous: This treatment strategy prevents all settlement in the system. Although 100 percent mortality doesn't occur, the presence of a noxious substance is enough to discourage zebra mussel veligers from settling. Adult mussels will either detach and attempt to leave the treated system or die if the lowlevel treatment is conducted throughout the entire reproductive season.

- Reactive strategies are used after zebra mussels have become established in a raw water system or have fouled external structures.

    - End-of-season: This treatment strategy is performed at the end of breeding season when mussels are most vulnerable and is applied to systems that can tolerate one season of fouling. Chemical is applied for a sufficient period of time to kill all adult mussels in the system. During and after the treatment, adult mussels will be released from the walls of the system.
    - Periodic: This strategy targets adult mussels on a regular basis. Treatment is usually conducted when densities and size of adult mussels are low so that debris removal is lessened. Systems must be able to tolerate some macrofouling.

Timing of Application

The efficiency of many strategies is enhanced if their timing is coordinated with veliger and mussel settlement data collection.

Generally, chemical controls to prevent settling and infestation need to be applied only during spawning periods, defined as water temperatures greater than 55 to 61 °F (12 to 16 °C).

Application Rates and Techniques

A wide range of concentration/exposure time combinations can be effective and are reported in the literature and in product information. This topic also includes special instructions for adding the compound to the system and maintaining it.

Maximum Water Concentrations

The Clean Water Act (CWA) requires that registered biocides discharged to waters of the United States from a point source must be regulated such that water quality-based effluent limits (WQBELs) for that biocide are established in a National Pollutant Discharge Elimination System (NPDES) permit to meet state water quality standards. There must also be compliance with each state's antidegradation policy. Thus, discharge limits of the chemical control compound depend on local, state, and Federal water restrictions as permitted under the NPDES program to regulate the amount of pollutants that may be discharged to waters by each discharger. Effluent guidelines are technology-based and are usually given on a case-by-case basis for individual facilities.

While commercial molluscicide labels may include specific NPDES discharge limits for that compound, many labels point out that the user must obtain an NPDES permit from the appropriate state/tribal agency or USEPA regional office and comply with state water quality requirements.

Products registered as pesticides by the USEPA must be handled and applied within the limits of the label instructions.

Although most molluscicides are biodegradable, some detoxification or deactivation may be required to meet state and Federal discharge requirements. See the topic "Adjuvant/Detoxicant/Deactivant Use."

Use Restrictions

Discharge restrictions and limitations on downstream use of treated water are discussed under this topic, along with permit requirements.

Timing of Results

This topic describes how rapidly zebra mussels are affected and whether or not monitoring may be required.

Toxicological Data

Signal Word: The USEPA-assigned signal word indicates approximately how toxic a pesticide product is. Products that are highly toxic must display on the label the signal words DANGER-POISON along with a skull and crossbones symbol. Products that display only the signal word DANGER are corrosive and can cause irreversible eye damage or severe skin injury. Products that display the signal word WARNING are moderately toxic or can cause moderate eye or skin irritation. Products that display the signal word CAUTION are slightly toxic or may cause slight eye or skin irritation.

Aquatic toxicology: Data for the effects of the compound on various freshwater organisms. Aquatic toxicity levels are usually reported as LC_{50}, which is the concentration lethal to 50 percent of test organisms.

Precautions

This topic gives pertinent information on precautions to take when handling the compound in its undiluted and dilute states. Also refer to MSDS for personal protective equipment information.

Adjuvant/Detoxicant/Deactivant Use

Although most molluscicides are biodegradable, some detoxification or deactivation may be required to meet state and Federal discharge requirements. Deactivation compounds may be recommended or be required by the label during molluscicide use or before discharge.

Proprietary deactivants or detoxicants are available. Bentonite clay in a dry or slurry form is a standard agent for several of the nonoxidizing compounds, added to the system discharge upstream of its outlet to the

environment. Binding properties of the clay generally render the biocide inactive.

Antidote Information

This topic gives brief emergency instructions, including phone numbers for companies that can supply treatment information.

References

Technical references for additional information are provided for each molluscicide.

Additional Chemicals and Treatments

Numerous pesticide compounds, in addition to the ones presented in this guide, have been suggested or investigated for zebra mussel control and are discussed in a variety of research and product information literature. The most common ones are summarized below.

Ammonium Nitrate

Ammonium nitrate is a nonoxidizing chemical that has been reported to kill adult zebra mussels in five to six days at rates of 400 to 500 mg L^{-1}. Ammonium nitrate could be used in closed loop systems or under agricultural circumstances where it is already being applied as a fertilizer. It is not feasible for once-through systems (Mackie and Claudi 2010).

Antifouling and Foul-Release Coatings

Antifouling coatings have biocides or metals incorporated into them, preventing zebra mussels from attaching to structures exposed to lake water (Wells and Sytsma 2009; Mackie and Claudi 2010). A common metal incorporated into antifouling coatings is copper. Coatings containing heavy metals, such as copper, are durable and effective but release biocide into the water impacting non-target aquatic fauna and can oxidize over time, thereby reducing effectiveness (Wells and Sytsma 2009; Chakraborti et al. 2014).

Foul-release coatings work by the hydrolysis of polymers that minimize initial attachment and strength of attachment or remove fouling with an eroded coating layer (Wells and Sytsma 2009). They work best in areas of

moderate to high flow (Mackie and Claudi 2010). Foul-release coatings are effective but can be mechanically weak, failing due to abrasion and detachment (Chakraborti et al. 2014). The most promising coatings contain silicone, which is nontoxic (Mackie and Claudi 2010). Silicone-based, foul-release coatings have an effective life span of six years and can cost about \$127 m^{-2} over a five year period (Wells and Sytsma 2009). According to the U.S. Bureau of Reclamation (USBR 2012), silicone-based coatings are effective for mussel control on infrastructure components that do not have gouges, debris or wear. Due to the limited life span of silicone-based coatings, surfaces will require periodic recoating (Chakraborti et al. 2014).

This is only a brief summary of antifouling and foul-release coatings. For more information or information on specific coatings, see reports by the USBR (2012 and 2014) and Wells and Sytsma (2009) listed in the references section.

BioBullets

Zebra mussels can sense oxidizing chemicals and other toxins and respond by closing their shells. BioBullets® are a new technology in which the active ingredient is encapsulated in an edible food-grade coating. The coating prevents zebra mussels from detecting the oxidizing chemical and their shells remain open. The individual particles are then filtered and digested by zebra mussels. The filtered particles are then concentrated within the bivalves resulting in lower concentrations of biocide needed for the system. An additional advantage to this technology is that more active ingredient is filtered out of the water and less ends up in the environment. Almost any biocide can be incorporated into BioBullets® and they are currently available in the United Kingdom (U.K.) (Aldridge et al. 2006; Mackie and Claudi 2010; Costa et al. 2012).

Ferrate

Ferrate, also known as iron oxide, is an oxidant/disinfectant that is powerful and environmentally safe. It is thought to not have any carcinogenic/mutagenic by-products and has been suggested as a possible treatment for macrofouling. To date, there are no protocols in place for using ferrate to control zebra mussel veligers or adults, but it is being evaluated (Mackie and Claudi 2010).

Hydrogen Peroxide

The oxidant hydrogen peroxide has been shown to effectively control zebra mussel veligers and adults; however, due to the high doses required for control, it is not considered a cost-effective treatment strategy (Van Benschoten et al. 1993b; Mackie and Claudi 2010).

Ozone

Ozone is an extremely strong oxidant that has been used in Europe for many years as a drinking water disinfectant (Van Benschoten et al. 1993a). Ozone improves the color, odor, and taste of drinking water and can be used to prevent biofouling (Mackie and Claudi 2010). Van Benschoten et al. (1993b) report that ozone is similar to chlorine at effectively removing zebra mussel veligers from the water column. At doses above 0.1 mg L^{-1}, veliger numbers were reduced by over 97 percent. Five hours of continuous exposure to 0.5 to 1.0 mg L^{-1} ozone at 18 to 20 °C is required for complete mortality of veligers. Ozone is also similar to chlorine at effectively killing adult zebra mussels at rates of 0.5 mg L^{-1} or greater (Van Benschoten at al. 1993a; Mackie and Claudi 2010).

Ozone molecules are relatively unstable and dissipate quickly in water (actual rate of dissipation is dependent on pH, temperature, and organic matter), thereby ensuring little to no end of pipe residual and no adverse environmental impacts (Mackie and Claudi 2010). The relatively short half-life of ozone can also be a major drawback because more chemical and longer contact times are required to maintain ozone concentrations (Mackie and Claudi 2010; Chakraborti et al. 2014). Another disadvantage to using ozone is the high initial equipment cost and the difficulties in maintaining it (Mackie and Claudi 2010). Examples of using ozone to control dreissenid infestations are given in Mackie and Claudi (2010).

USEPA Registration of Chemical Molluscicides

Chemical pesticides can be an important tool to control infestations of invasive mollusks. However, an understanding of the regulatory and legal standing of pesticide compounds such as molluscicides is mandatory in handling and applying these products. Howe et al. (1994) and Burns (1994) describe how the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA), enacted in 1972, governs the registration and use restrictions of chemicals for molluscicides, including those used for zebra mussel

control. The act monitors chemicals intended for control of living organisms and, as amended, requires registration and re-registration by the USEPA of pesticides sold or used in the U.S. to ensure that they will not cause unreasonable risk to the environment or human health when used according to the label directions. These regulations then apply to anyone who manufactures, formulates, markets, distributes, uses, or disposes of pesticide products, including aquatic biocides that would be used as molluscides. Moreover, most states require their own specific registration of pesticides in addition to registration with the USEPA. State-registered use patterns can be more restrictive than the Federal registration, but not less restrictive.

The primary registration mechanism is governed by FIFRA Section 3. Applications for registration of molluscicides may be for new active ingredients, the new use of a previously registered pesticide, or chemicals similar to currently registered compounds. The registration process (paid for by the registrant) is generally expensive (multi-millions of dollars) and tedious (5 to 10 years) because it requires detailed research and evaluations by the registrant to determine efficacy, effective use rates, and any environmental side effects of the active ingredient. Aquatic use pesticides have the highest level of toxicity testing of any pesticides. Some of this testing is carried out in field settings via Experimental Use Permit (EUP) provisions under FIFRA Section 5. This field testing may delay or prevent approval for use of the compound in a specific state. The expense and time of acquiring registration for biocidal compounds has slowed the discovery and marketing process of new chemicals specifically for the niche area of zebra mussel control, compared to agricultural row-crop uses of pesticides.

The effect of discharge water containing molluscicidal chemicals on downstream receiving waters must be considered prior to the formulation of a treatment program. Even with discharge limits and requirements and the use of deactivation of the active ingredient, there may be an effect on the ecosystem that needs to be avoided, or it may be necessary to restrict treatment to certain times of the year (Claudi and Evans 1993). The legislation currently used to control direct discharges to waters of the U.S. is the NPDES permit program. This was made possible by the passage of the Federal Water Pollution Control Act Amendments of 1972, also referred to as the CWA. These permits place limits on the amount of pollutants that may be discharged to water by each discharger. Limits are set at levels protective of both the aquatic life in the waters that receive the discharge

and human health. The CWA requires that registered biocides discharged to waters of the U.S. from a point source must be regulated such that WQBELs for that biocide are established in an NPDES permit to meet state water quality standards. There must also be compliance with each state's antidegradation policy. Thus, one of the label requirements for use of many aquatic biocides and pesticides in aquatic environments is to obtain an NPDES permit from the appropriate state/tribal agency or USEPA regional office and to comply with state water quality requirements. Lack of a permit could result in enforcement action under FIFRA and the CWA. A risk-benefit analysis is also carried out by the USEPA, and a pesticide can be designated for "restricted use" if it is judged as presenting a high risk to humans or the environment. States usually require these chemicals to be applied only by trained and certified applicators or people in their employ.

As well as FIFRA Section 3 registration, conditional use of pesticides may be authorized through Special Local Needs (SLN) under Section 24(c); through Emergency Exemptions (Section 18); or through EUP provisions under Section 5. Use of a registered product on a pest not listed on the product label is allowed under Section 2(ee) as long as application is to a site stated on the label (Howe et al. 1994). However, specific registration for use in once-through cooling systems is required in many water handling operations where mussels are treated in these areas (Claudi and Mackie 1994). Any direct in-water use of a molluscicide under an EUP is limited to a negotiated, annual acreage by the registrant and the USEPA, and these permits are designed to refine use patterns and efficacy under real-world field conditions. A non-registered molluscicide can be used without a permit in aquatic sites for efficacy evaluations, but no more than one surface acre, per pest species, per year is allowed.

It is important to remember that the product label of a registered pesticide is a legal document. Use of an aquatic biocide or molluscicide in a way that is inconsistent with the instructions provided on the label is a violation of FIFRA and can result in civil or even criminal action, via proceedings from the USEPA under FIFRA or from certain states (Howe et al. 1994). Also, compliance with the National Environmental Policy Act (NEPA) is required if Federal funds are used for zebra mussel control. This legislation dictates that control methods used at public facilities must not negatively affect native biota or existing water quality (Miller et al. 1992). A protocol for compliance with the NEPA process that should be used in developing chemical control strategies for zebra mussels is described by

Miller et al. (1992), and a working plan is reported on by Tippit et al. (1993). Finally, if a Federal nexus (waters, personnel, funding) is determined for aquatic field treatments, consultation with the USFWS is required (at a minimum) to ensure that applications are not likely to adversely impact any listed species (threatened or endangered) in the treatment area.

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2 Chlorination

The cost-effective activity of chlorination has made it the most commonly used compound for all types of water disinfection and biofouling control in North America, and it has been used in potable water treatment for over 100 years (Mackie and Claudi 2010). Chlorination, primarily via sodium hypochlorite, has dominated the chemical control of zebra mussels in both Europe and North America, and remains the least expensive and most popular method of removal. Chlorination effects can be provided by a range of compounds to control zebra mussels and related nuisance mollusk species. Chlorine compounds include: the hypochlorites of sodium, potassium, or calcium, chlorine, and chlorine dioxide gases, and sodium chlorite. Due to safety concerns, the use of chlorine gas is discouraged in North America and most industries have switched to sodium hypochlorite (Mackie and Claudi 2010).

Chlorine not only has a direct toxic effect on adult zebra mussels, but also weakens the mussels' attachment to substrates and inhibits settlement and growth of veligers (Mackie and Claudi 2010). In general, chlorine treatment for zebra mussel control is dependent on the quantity and type of chlorine compound used, chlorine concentration and exposure time, water quality parameters (pH, temperature, presence of organic and inorganic compounds), and the physical state of the mussels at the time of treatment (Mackie and Claudi 2010).

Mackie and Claudi (2010) discuss chlorination processes for zebra mussel control in industrial systems in detail, along with associated pros and cons. Chlorine has a number of important advantages: it is relatively inexpensive, it works in most raw water systems, it is toxic at low concentrations and quickly loses toxicity without bioaccumulating, and it can be applied with basic techniques. However, there are several drawbacks to the chlorination process. The transport and storage of gaseous or liquefied chlorination products involve hazards, so they require special handling. Discharge also presents problems because carcinogenic compounds known as trihalomethanes may be formed where organic compounds are present in water. Differences in water quality may lead to extra costs where discharge concentrations are unpredictable due to varying chlorine demand.

The next section reviews the general properties of chlorination via hypochlorite. Unless stated otherwise, information in the following section is summarized from Mackie and Claudi (2010). Chlorine dioxide is discussed separately.

Hypochlorite and Chlorine Gas

Chemical Name and Formulations

Chlorination compounds are available from numerous commercial sources as the following chemicals:

- Calcium hypochlorite, $Ca(OCl)_2$; solid
- Sodium hypochlorite, NaOCl; liquid; 12 percent available chlorine by weight is most commonly used by industry
- Potassium hypochlorite, KOCl; liquid
- Chlorine, Cl_2; gas

Mode of Action

Chlorine controls zebra mussels through the effects of oxidation, consisting of either direct toxic effects on the adult, inhibition of settlement and growth of the larval stage, or weakening of the byssal thread attachments. Toxicity of chlorine to zebra mussels is dependent on the concentration, exposure time, and type and quantity of chlorine compound formed in water following treatment.

Hypochlorite reacts with water to form hypochlorous acid (HOCl), which readily dissociates to hydrogen ions (H^+) and hypochlorite (OCl^-).

$$NaOCL + H_2O \leftrightarrow HOCL + Na^+(OH)^+$$

$$HOCl \leftrightarrow H^+ + OCl^-$$

The dissociation of the hypochlorite ion is pH dependent. For example, at pH 8.5, half of the chlorine present will be undissociated hypochlorous acid and half will be the hypochlorite ion. The hypochlorous acid is a more effective biocide due to its ability to penetrate cell walls easily. Together, hypochlorous acid and the hypochlorite ion make up the *free available chlorine* (FAC).

These FAC compounds react with ammonia and other nitrogen-containing compounds to make chloramines, which also contribute to disinfection and are known as the *total combined chlorine* (TCC). The combination of FAC and TCC is the *total residual chlorine* (TRC). The presence of organic nitrogen and other compounds reduces TRC because chlorine forms complex nitrogen compounds. Additional chlorine must be added to obtain a desired TRC level, and this differential, called *chlorine demand*, varies with type of raw water and season.

Application Strategies

The following four treatment strategies can be used for controlling zebra mussels via chlorination:

- End-of-season treatment: This treatment is given to flush out relatively small amounts of accumulated adults. Because there will be a large release of shell and soft tissue debris, some method of handling the debris needs to be in place. Byssal threads will remain after the dead mussel has sloughed off. These remaining byssal threads can serve as an easy attachment site for the next year's veligers and can cause under-deposit corrosion. This treatment typically occurs between mid-August and mid-September in the Great Lakes region.
- Periodic treatment: The goal of this strategy is to regularly eliminate all mussels from the system during the breeding season. Zebra mussels are smaller during this time and therefore less debris is generated. A disadvantage to this strategy is the greater amount of labor and chlorine required.
- Intermittent treatment: This strategy is meant to prevent zebra mussel establishment. Post-veligers easily pass through the system eliminating debris problems, and under-deposit corrosion is avoided because adults are unable to colonize. This treatment is not effective against established adults.*
- Semicontinuous treatment: Frequent on/off cycling of treatment can have effects similar to continuous chlorination. This treatment has a lower cost of material due to reduced exposure time. Also, because portions of a facility are treated at one time, there is more dilution water available, which can help meet discharge limits.
- Continuous treatment: When chlorine is applied continuously, veligers that enter a system can sense the chemical and keep their shells closed, thereby passing through the system without attempting to settle. Because a continuous treatment adds more total chlorine to receiving

waters than intermittent or semicontinuous treatments, it is more appropriate for small, critical subsystems.

*Adult zebra mussels can be controlled if Pulse-chlorination® is used. Adult mussels close their shells when chlorine is detected and resume normal feeding (after a lag time) when chlorination is stopped, which is why the traditional intermittent treatment strategy is not effective against adult mussels. The Pulse-chlorination® technology takes advantage of the lag time between when chlorination is halted and when normal filter feeding resumes. Just before normal feeding resumes, chlorination is resumed. The mussels experience continuous chlorination even though the treatment is intermittent (Rajagopal et al. 2003).

Timing of Application

If a single, long-term application is being used to kill all mollusks present, it should be made following the reproduction period to ensure that no additional veliger settling will occur. Reproduction in zebra mussels is also dependent on water temperature, and this timing will be keyed in to the time of year.

A one-time end-of-season application can be done if the infestation is low enough that debris will flush out without blocking the system. If the infestation is large and will block any part of the system, then periodic applications may be required.

For veliger control, there is no need to chlorinate during winter when temperatures are too low for reproduction. Chlorination can also be suspended during periods when veligers are not present in intake water.

Application Rates and Techniques

- End-of-season treatment: At a rate of 0.65 mg L^{-1} TRC, 100 percent mortality can be achieved in 10 to 14 days.
- Periodic treatment: This treatment requires approximately the same or slightly less chlorine than the end-of-season treatment.
- Intermittent treatment: A standard treatment is 2 mg L^{-1} TRC for 1.5 hours at 12 hour intervals.
- Semicontinuous treatment: A rate of 0.5 mg L^{-1} applied for 15 minutes on and 15 to 30 minutes off is as effective as a continuous treatment.

This treatment should be applied to an entire breeding system in order to kill adults already in the system and prevent new settlement.

- Continuous treatment: A 90-day continuous treatment of 0.5 mg L^{-1} TRC has been shown to prevent new settlement, but also to kill adult mussels already in the system. A 0.3 mg L^{-1} TRC has been reported to be just as effective as the 0.5 mg L^{-1} rate.

Maximum Water Concentrations

Discharge limits for specific facilities depend on local, state, and Federal water restrictions as permitted under the NPDES program.

The USEPA National Primary Drinking Water Regulations (2009) set the following maximum contaminant levels (MCL) and maximum residual disinfectant levels (MRDL):

- Chloramine (as Cl_2): 4.0 mg L^{-1} MRDL
- Chlorine (as Cl_2): 4.0 mg L^{-1} MRDL
- Chlorite: 1.0 mg L^{-1} MCL
- Total trihalomethanes: 0.08 mg L^{-1} MCL

Use Restrictions

See Maximum Water Concentrations section.

Timing of Results

Resistance to chlorine can vary with age, size, and developmental stage of the mussel, with older and larger individuals being more resistant. Veligers are much more susceptible than adults.

Considerable lag times between application and adult zebra mussel death have been observed, presumably due to shell closure when the presence of oxidant is sensed. Lag times can range from 2 to 18 days (Van Benschoten et al. 1993).

Toxicological Data

Signal Word: Danger

Toxicity data for sodium hypochlorite to aquatic species is shown in Table 1.

Table 1. Toxicity of sodium hypochlorite (5% Chlorine[1]) to aquatic species.

Organism	Test	Result
Freshwater Algae	24 hr EC_{50}	0.095 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50}	0.82-0.98 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr EC_{50}	0.033-0.044 mg L^{-1}
Water Flea (*Daphnia magna*)	96 hr EC_{50}	2.1 mg L^{-1}

[1] From MSDS (ACROS Organics 2012)

Precautions

- Irritating to eyes, skin and respiratory system.
- May be harmful if swallowed.
- Ensure adequate ventilation.
- Store in well-ventilated, dry, cool place away from light.

Adjuvant/Detoxicant/Deactivant Use

Dilution is the most common means of detoxification.

For facilities that cannot achieve discharge limits via dilution, neutralizing chlorine with sodium sulfite, sulfur dioxide, or sodium bi or metabisulfite must be done. “Liquid sulfite” is a commercially available sodium bisulfite solution. Use 1.8 to 2.0 mg L^{-1} of sulfite per mg L^{-1} residual chlorine, reaction is rapid.

Antidote Information

The following information is from the MSDS for sodium hypochlorite (5 percent chlorine; ACROS Organics 2012):

- Eyes: Immediately rinse for at least 15 minutes using plenty of water. Make sure to rinse under the eyelids. Obtain medical attention.
- Skin or clothing: Immediately wash off with plenty of water for at least 15 minutes. Obtain medical attention.
- Ingestion: Do not induce vomiting. Obtain medical attention.
- Inhalation: Move to fresh air. Give oxygen if breathing is difficult. Obtain medical attention.
- Emergencies: ACROS at 201-796-7100 or CHEMTREC at 1-800-424-9300

References

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Chlorine Dioxide

Chlorine dioxide (ClO_2) is a powerful disinfectant used in the water treatment industry for over 50 years. Several advantages to using chlorine dioxide include: its effectiveness at all pH levels, it does not react with ammonia to form chloramines, it does not produce trihalomethanes (THM), it is effective at low concentrations and it requires only short treatment durations (Fisher et al. 2003; Mackie and Claudi 2010). Some reports indicate chlorine dioxide is more effective than chlorine in reducing post-veliger settlement (Rusznak et al. 1995) and increasing adult zebra mussel mortality (Matisoff et al. 1996). Disadvantages include: the requirement for on-site generating equipment, storage of chemical precursors and the conversion of chlorine dioxide to chlorite, which limits the amount of chlorine dioxide that can be applied without excessive chlorite discharge (Mackie and Claudi 2010; Fisher et al. 2003).

Chemical Name and Formulations

Chlorine dioxide is a pale yellow water-soluble gas at room temperature. The generic chemical is available from numerous commercial sources.

Mode of Action

Chlorine dioxide is an oxidizing agent which causes membrane damage.

Application Strategies

Recommended application is by injection of chlorine dioxide gas manufactured on-site using temporary or permanently installed generation and detoxification equipment. Chlorine dioxide can be made from precursors such as the following:

- Sodium chlorite + chlorine gas
- Sodium chlorite + hydrochloric acid
- Sodium chlorate + hydrogen peroxide + sulfuric acid
- Sodium chlorite + sodium hypochlorite + hydrochloric acid

Some chemical manufacturers can produce 3000 ppm solutions of chlorine dioxide for delivery to the site. Although chlorine dioxide is not classified as hazardous, it can sublimate to an extremely poisonous gaseous phase at room temperature. Equipment must be airtight and closely monitored to avoid safety and health concerns (Mackie and Claudi 2010).

Timing of Application

Chlorine dioxide can be applied as an intermittent or continuous treatment.

Application Rates and Techniques

Examples of effective treatments are described below:

- Intermittent:
    - 0.25 ppm for 15 minutes at 6-hour intervals at 12.8 °C resulted in a 95 percent reduction in post-veliger settlement (Rusznak et al. 1995)
    - 10 to 20 ppm applied for 30 minutes a day for 3 to 7 consecutive days induced significant mortality of adult zebra mussels (Matisoff et al. 1996)

- Continuous:
    - 0.45 ppm ClO_2 for 145.5 hours (~ 6 days) at 17 °C resulted in 100 percent mortality of adult zebra mussels (Holt and Ryan 1997)

- Periodically applying 1 ppm ClO_2 for 4 days is effective to kill adult zebra mussels (Matisoff et al. 1996)
- 0.15 to 0.5 ppm above the oxidant demand for 2 to 4 days can effectively eradicate adult zebra mussels (Smolik et al. 1995)

Chlorine dioxide readily dissolves in water.

Maximum Water Concentrations

Discharge limits depend on local, state and Federal water restrictions as permitted under the National Pollutant Discharge Elimination System program.

Use Restrictions

Restrictions involve the MCL based on the sum of residual chlorine dioxide, chlorate and chlorite (Van Benschoten et al. 1993).

Timing of Results

Considerable lag times between application and adult zebra mussel death have been observed, presumably due to shell closure when the presence of oxidant is sensed. Lag times can range from 2 to 18 days (Van Benschoten et al. 1993). Time to death is dependent on the rate and exposure time of chlorine dioxide as well as temperature. The data in Table 2 taken from Holt and Ryan (1997) demonstrates this.

Table 2. Chlorine dioxide toxicity to adult zebra mussels.

Concentration (mg L^{-1})	Hours to 100% mortality at 14.3 °C	Hours to 100% mortality at 25.8 °C
0.25	211	89
0.5	139	40
1.0	102	--
2.0	78	--
5.0	70	--

Toxicological Data

Signal Word: Danger

Toxicity data for chlorine dioxide to aquatic species is shown in Table 3.

Table 3. Toxicity of 5 % stabilized chlorine dioxide[1] to aquatic species.

Organism	Test	Result
Sheepshead Minnow (*Cyprinodon variegatus*)	96 hr LC_{50}	105 mg L^{-1}
Freshwater Algae (*Scenedesmus capricornutum*)	96 hr EC_{50}	1 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr EC_{50}	<1 mg L^{-1}
Mysid Shrimp (*Americamysis bahia*)	96 hr LC_{50}	0.65 mg L^{-1}

[1] From MSDS (DuPont 2012)

Chlorine dioxide is reduced to chlorite (ClO_2^-) and chloride (Cl^-) ions. Chlorite is stable once formed and toxicity data for this ion to aquatic species is shown in Table 4.

Table 4. Toxicity of chlorite[1] to aquatic species.

Organism	Test	Result
Water Flea (*Daphnia magna*)	96 hr LC_{50}	0.039 mg L^{-1}
Crayfish (*Procambarus clarkii*)	96 hr LC_{50}	1.27 mg L^{-1}
Bluegill (*Lepomis macrochirus*)	96 hr LC_{50}	53.14 mg L^{-1}
Toad (*Bufo americana*)	96 hr LC_{50}	149.60 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50}	63.38 mg L^{-1}
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	208.76 mg L^{-1}

[1] From Fisher et al. (2003)

Precautions

- Avoid contact with eyes, skin and clothing.
- Only use in well-ventilated areas.
- Store in a cool, dry, and well-ventilated area. Keep away from strong acids and oxidizing agents. Avoid exposing product to freezing, heat and Ultraviolet (UV) light.
- Do not allow product to dry.
- Corrosive, can cause severe skin, eye and respiratory tract irritation.

Adjuvant/Detoxicant/Deactivant Use

Sodium bisulfite has been used to neutralize chlorine dioxide and residual oxidants at discharge locations. For every 1 ppm of oxidant, 7 ppm of dechlorinating agent is needed (Tsou et al. 1995).

Antidote Information

The following information is from the MSDS for 5 percent stabilized chlorine dioxide (DuPont 2012):

- Eyes: Immediately rinse with plenty of water. Seek medical advice.
- Skin and clothing: Immediately remove contaminated clothing and shoes. Wash off with plenty of water. Call a doctor or poison control center for treatment advice.
- Inhalation: Move to fresh air. Give artificial respiration if not breathing. Call a doctor or poison control center for treatment advice.
- Emergencies: 1-800-441-3637

References

DuPont. 2012. Material Safety Data Sheet: 5% Stabilized chlorine dioxide. Wilmington, DE.

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Smolik, N., L. Rusznak, J. Anderson, and L. Hale. 1995. The use of chlorine dioxide for zebra mussel control – A perspective of treatment histories. In *Proceedings of the Fifth International Zebra Mussel and Other Aquatic Nuisance Organisms Conference 1995, 14-21 February, Toronto, Canada.*

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Van Benschoten, J. E., J. N. Jensen, D. Lewis, and T. J. Brady. 1993. Chemical oxidants for controlling zebra mussels (*Dreissena polymorpha*): A synthesis of recent laboratory and field studies. In: *Zebra Mussels: Biology, Impacts, and Control*, ed.T. F. Nalepa and D. W. Schloesser, 599-619. Boca Raton, FL: Lewis Publishers,.

3 Nonchlorine Oxidizing Chemicals

In addition to chlorinating chemicals, the oxidizers ammonia, bromine, and potassium permanganate can be used for treatment of zebra mussels.

Ammonia

FAC compounds react with ammonia or other nitrogen-containing compounds to form chloramines. Although chloramines are a less powerful oxidant, concentrations above 1.5 mg L^{-1} have been shown to kill 90 percent of zebra mussel veligers. Monochloramine, formed when ammonia reacts with sodium hypochlorite, has been used as a drinking water disinfectant and as an Asian clam veliger control measure (Van Benschoten et al. 1993; Mackie and Claudi 2010).

Oxamine® 6150

Oxamine 6150 is used in conjunction with sodium hypochlorite to form monochloramine, which is a less aggressive and slower acting oxidizing biocide (Buckman Laboratories, Inc. 2011). It is stable over a wide range of pH, has long-lasting residual effectiveness, and degrades to nontoxic minerals. There is no formation of organic by-products (Buckman Laboratories, Inc. 2014b).

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: ammonia
- Formulation: Oxamine® 6150
    - 7.59 percent active ingredient
    - Liquid
- USEPA registration number 1448-433
- Source: Buckman Laboratories, Inc.
  1256 North McLean Boulevard
  Memphis, TN 38108
  1-800-282-5626
- Synonyms: BUSAN® 1215

Mode of Action

See Mode of Action section for hypochlorite and chlorine gas.

Application Strategies

This product can be used for intermittent or continuous treatments.

Timing of Application

This product can be applied any time sodium hypochlorite is applied.

Application Rates and Techniques

Oxamine® 6150 is applied in conjunction with sodium hypochlorite to form monochloramine. The monochloramine solution must be generated and fed via a closed metered chemical feed system.

Badly fouled systems must be cleaned before initial treatment.

Intermittent treatment: Mix 0.5 fluid ounces of this product to 1.0 fluid ounce of sodium hypochlorite. Apply this solution at a rate of 1 to 2 ppm, in excess of the system oxidant demand as total chlorine in water being treated. Treat for 5 to 60 minutes every 1 to 6 hours. Frequency and duration depend on severity of the problem.

Continuous treatment: Mix 0.5 fluid ounces of this product to 1.0 fluid ounce of sodium hypochlorite. Apply this solution at a rate of 0.5 to 1 ppm in excess of the system oxidant demand as total chlorine in water being treated on a continuous basis.

Contact a company representative for more information.

Maximum Water Concentrations

If chloramines are detected in the effluent, it must be neutralized with sodium metabisulfite until chloramines are no longer detected.

Use Restrictions

This product is toxic to fish and aquatic organisms.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority.

Timing of Results

Considerable lag times between application and adult zebra mussel death have been observed, presumably due to shell closure when the presence of oxidant is sensed. Lag times can range from 2 to 18 days (Van Benschoten et al. 1993).

Toxicological Data

Signal Word: Caution

Table 5 summarizes the toxicity of Oxamine® 6150 to aquatic species.

Table 5. Toxicity of Oxamine® 6150[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	≥ 126 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	≥ 117 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	≥ 131 mg L^{-1}

[1] From MSDS (Buckman Laboratories, Inc. 2014a)

Precautions

- Avoid contact with eyes, skin, or clothing.
- Avoid breathing vapor.
- Harmful if swallowed.
- Remove and wash contaminated clothing before reuse.

Adjuvant/Detoxicant/Deactivant Use

Sodium metabisulfite can be added if chloramine is detected in effluent.

Antidote Information

The following information is from the MSDS for Oxamine® 6150 (Buckman Laboratories, Inc. 2014a):

- Eyes: Flush eyes with tap water or normal saline for a minimum of 15 minutes. Seek medical attention, preferably an ophthalmologist.
- Skin or clothing: Wash exposed area with plenty of water. Repeat washing. Remove contaminated clothing and wash before reuse. If irritation persists, seek medical attention.
- Ingestion: Do not induce vomiting. Irrigate esophagus and dilute stomach contents by slowly giving 1 to 2 glasses of water or milk. Do not give fluids by mouth if individual is semi-comatose, comatose, or convulsing. Seek immediate medical attention.
- Inhalation: Immediately move exposed individual to fresh air. Seek medical attention if individual experiences headache, nausea, dizziness, difficulty breathing, or is cyanotic.
- Emergencies: 901-767-2722

References

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Van Benschoten, J. E., J. N. Jensen, D. Lewis, and T. J. Brady. 1993. Chemical oxidants for controlling zebra mussels (*Dreissena polymorpha*): A synthesis of recent laboratory and field studies. In: *Zebra Mussels: Biology, Impacts, and Control*, ed.T. F. Nalepa and D. W. Schloesser, 599-619. Boca Raton, FL: Lewis Publishers.

Bromine

Bromine is an oxidizing chemical that is used for antifouling purposes in such forms as activated bromine, sodium bromide, bromine chloride, and mixtures of bromine and chlorine or other chemicals (Mackie and Claudi 2010). Bromine is approved for use in the U.S. for zebra mussel control. It

is more effective as an oxidizing agent when water pH is above 8.0 (Fellers et al. 1988). Bromine is also used as a chlorine enhancer designed to minimize the amount of chlorine required to prevent macrofouling; several proprietary compounds are used in this way.

In the past, it was suggested that bromine was less toxic than chlorine to nontarget species, but this has been shown not to be the case (Howe et al. 1994). The total amount of oxidant required for mussel control is approximately the same as chlorine (Mackie and Claudi 2010).

Chemical Name and Formulations

Two examples of sodium bromide ($NaBr_2$) are characterized as follows:

- ACTI-BROM® 1338 Chlorine Enhancer & Biodispersant
    - 42.8 percent active ingredient
    - Liquid
    - USEPA registration number 1706-168
    - Nalco Company
      1601 West Diehl Rd.
      Naperville, IL 60563-1198
      630-305-1000

- SPECTRUS® OX1201
    - 40 percent active ingredient
    - Liquid
    - USEPA registration number 3876-159
    - GE Betz, Inc.
      4636 Somerton Rd.
      Trevose, PA 19053
      215-355-3300
      Mode of Action

ACTI-BROM® 1338 (Nalco Company 2012) and SPECTRUS® OX1201 (GE Betz, Inc. 2010) utilize a chlorine source to activate a bromide/ biodispersant chemistry. In the presence of chlorine gas or sodium hypochlorite, the bromine portion of these products is activated to form hypobromous acid and hypobromite ion, depending on water pH (Fellers et al. 1988). Both of these forms of bromine are lethal to zebra mussels.

Hypochlorous acids are also formed, and the ratio of hypobromous acid to hypochlorous acid can be varied by altering the molar ratios between the chlorine source and sodium bromide-surfactant (McCarthy and Trulear 1992).

$$Cl2 + H2O \rightarrow HOCl + HCl$$

or

$$NaOCl + H2O \rightarrow HOCl + NaOH$$

then

$$HOCl + NaBr \rightarrow HOBr + NaCl$$

The surfactant (biodispersant) does not contribute to toxicity but may inhibit biofilm deposition, which is a necessary precursor to zebra mussel veliger attachment (McCarthy and Trulear 1992).

Application Strategies

These products can be used to control and prevent the settlement of zebra mussels.

Timing of Application

Can be applied whenever chlorine is applied.

Application Rates and Techniques

Dosage rates range from 0.125 to 2.0 sodium bromide/oxidant mole ratio. See below examples.

ACTI-BROM® 1338

- 1.8 to 29.0 pounds of chlorine gas (99.9 percent) per gallon of sodium bromide solution
- 1.4 to 23.2 gallons sodium hypochlorite (12.5 percent available chlorine) solution per gallon of sodium bromide solution

SPECTRUS® OX1201

- 1.6 to 26.5 pounds of chlorine gas (99.9 percent) per gallon of sodium bromide solution

- 1.3 to 21.2 gallons sodium hypochlorite (12.5 percent available chlorine) solution per gallon of sodium bromide solution

Consult company representatives for specific dosages as they will vary depending on the level of fouling, water chemistry, and operating system.

Maximum Water Concentrations

These products are registered as pesticides by the USEPA and must be handled and fed within the limits of the label instructions.

Use Restrictions

Do not discharge effluent containing either product into streams, lakes, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit. Prior to discharge, the permitting authority must be notified in writing.

Do not discharge effluent containing either product into sewage systems without prior notification to the local sewage treatment authority.

Timing of Results

Effect is synchronous with chlorine co-treatment effect. It produces more rapid effects in veliger stages than in adults.

Toxicological Data

Signal Word: Caution

Toxicity data for bromine to aquatic species is shown in Table 6.

Table 6. Toxicity of sodium bromide (as ACTI-BROM® 1338 and SPECTRUS® OX1201) and bromine to aquatic species.

Toxicity of ACTI-BROM® 1338[1]		
Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	>1,000 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	>1,000 mg L^{-1}
Fathead Minnow (*Pimephales promelus*)	96 hr LC_{50}	>1,000 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	>1,000 mg L^{-1}
Mysid Shrimp (*Mysidopsis bahia*)	96 hr LC_{50}	1,827 mg L^{-1}

Toxicity of SPECTRUS® OX1201[2]		
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	≥1000 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	≥1000 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	27,500 mg L^{-1}
Toxicity of Bromine[2]		
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	0.23 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	0.52 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	0.71 mg L^{-1}

[1] From MSDS (Nalco Company 2011)

[2] From MSDS (GE Betz, Inc. 2012)

Precautions

- ACTI-BROM® 1338
    - Harmful if swallowed or absorbed through skin
    - Can cause moderate eye irritation
    - Avoid contact with eyes, skin and clothing
    - After handling, wash with soap and water
    - Wash contaminated clothing before reuse
- SPECTRUS® OX1201
    - May cause moderate eye irritation
    - Aerosols or mists may cause upper respiratory tract irritation
    - May cause skin itching or redness

Adjuvant/Detoxicant/Deactivant Use

ACTI-BROM® 1338 and SPECTRUS® OX1201 are used as adjuvants to chlorine treatments. Depending on outfall permits, deactivation with sodium bisulfite may be necessary. See specifics in chlorine section of this document.

Antidote Information

The following information is from the MSDS for ACTI-BROM® 1338 (Nalco Company 2011):

- Eyes: Holding the eye open, gently and slowly rinse with water for 15 to 20 minutes or until it's judged that nearly all of the contamination has been removed. If wearing contact lenses, remove them after the first five minutes and continue rinsing. Immediately call a doctor or poison control center for treatment advice.
- Skin or clothing: Remove contaminated clothing. Immediately rinse skin with plenty of water for 15 to 20 minutes. Call a doctor or poison control center for treatment advice.
- Ingestion: Immediately call a doctor or poison control center for treatment advice. Do not induce vomiting. Do not give anything to drink.
- Inhalation: Move person to fresh air. If person is not breathing, call 911 and then give artificial respiration. Call a doctor or poison control center for treatment advice.
- Emergencies: 1-800-424-9300

First-aid treatment varies slightly for SPECTRUS® OX1201, see MSDS for details.

References

Fellers, B. D., E. L. Flock, and J. C. Conley. 1988. Bromine replaces chlorine in cooling-water treatment. *Power* 132(6):15-20.

GE Betz, Inc. 2010. SPECTRUS OX1201 Master label. Trevose, PA. http://www.epa.gov/pesticides/chem_search/ppls/003876-00159-20100416.pdf. Accessed August 22, 2014.

GE Betz, Inc. 2012. Material Safety Data Sheet: SPECTRUS OX1201. Trevose, PA.

Howe, P. H., E. Masters, R. Atteberry, and P. Redmon. 1994. *A summary of Federal regulations related to use of FIFRA-registered biocides and Region 5, USEPA, use of these biocides for zebra mussel control*. Zebra Mussel Technical Note Collection. ZMR-1-15. Vicksburg, MS: U.S. Army Engineer Waterways Experiment Station,.

Mackie, G. L. and R. Claudi. 2010. *Monitoring and control of macrofouling mollusks in fresh water systems, second edition*. Boca Raton, FL: CRC Press.

McCarthy, R. E. and M. G. Trulear. 1992. Efficacy of an oxidizing molluscicide against zebra mussels: Results of laboratory and field studies. *Proceedings of Corrosion '92, NACE Annual Conference and Corrosion Show, Houston, TX, May 1992*.

Nalco Company. 2011. Material Safety Data Sheet: ACTI-BROM® 1338. Naperville, IL.

Nalco Company. 2012. ACTI-BROM 1338 Master label. Naperville, IL. http://www.epa.gov/pesticides/chem_search/ppls/001706-00168-20120607.pdf. Accessed August 22, 2014.

Potassium Permanganate

Potassium permanganate is a strong nonchlorine oxidant with a long history of safe use in drinking water, wastewater, and chemical manufacturing industries. It has been used by water treatment plants as an oxidizer since the turn of the 20th century, and is commonly used in municipal facilities for water purification. It is widely used to protect against oxidation of manganese and iron and to correct taste and odor problems in treated water (Mackie and Claudi 2010). Unlike chlorine, potassium permanganate does not produce trihalomethane, but at high concentrations it can give water a reddish color (San Giacomo and Wymer 1997). Although it can be used against zebra mussels, potassium permanganate is less effective than chlorine (Mackie and Claudi 2010).

Chemical Name and Formulations

One example of potassium permanganate is characterized as follows:

- 97 percent active ingredient
- Solid
- Chem One Ltd.
  14140 Westfair East Dr.
  Houston, TX 77041-1104
  713-896-9966

Mode of Action

Potassium permanganate has oxidizing activity. It has been observed that adult mussels retract their siphons while potassium permanganate is passing through the system.

Application Strategies

Potassium permanganate can be used to control adult zebra mussels as well as prevent veliger settlement (San Giacomo and Wymer 1997).

Timing of Application

Apply during zebra mussel growing season, especially during the veliger settling phase.

Application Rates and Techniques

Potassium permanganate is mixed with water to form a 2-to-5 percent solution before being injected into the water system (San Giacomo and Wymer 1997).

Adult zebra mussels can be controlled at concentrations up to 2 mg L^{-1}. Rates of less than 1 mg L^{-1} can control settling of veligers (San Giacomo and Wymer 1997).

Maximum Water Concentrations

Discharge limits depend on local, state, and Federal water restrictions as permitted under the NPDES program.

Use Restrictions

See Maximum Water Concentrations section.

Timing of Results

Treatment effects occur within days.

Mortality rates are dependent on oxidant demand, temperature, and contact time (San Giacomo and Wymer 1997).

Toxicological Data

Signal Word: Warning

Toxicity of potassium permanganate to aquatic species is listed in Table 7.

Table 7. Toxicity of potassium permanganate[1] to aquatic species.

Organism	Test	Result
Channel Catfish (*Ictalurus punctatus*)	96 hr LC_{50}	0.75 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	2.7 - 3.6mg L^{-1}
Milkfish (*Chanos chanos*)	24 hr LC_{50}	1.4886 mg L^{-1}
Goldfish (*Carassius auratus*)	96 hr LC_{50}	3.6 mg L^{-1}
Copepod (*Mesocyclops leuckarit*)	24 hr LC_{50}	2.45 mg L^{-1}

[1] From MSDS (Chem One 2009)

Precautions

- Avoid contact with skin and eyes as product can cause burns.
- May be fatal if inhaled or swallowed.
- Avoid breathing dusts; may irritate respiratory tract.
- Wash thoroughly after handling.
- Use adequate ventilation.
- Avoid contact with combustible materials.

Adjuvant/Detoxicant/Deactivant Use

None is specified.

Antidote Information

The following information is from the MSDS for Potassium Permanganate (Chem One 2009):

- Eyes: Immediately rinse eyes with water for at least 15 minutes. Seek medical attention if adverse reaction occurs.
- Skin or clothing: Remove contaminated clothing and wash with soap and water. If irritation develops, seek medical attention.
- Ingestion: Do not induce vomiting unless directed by physician. Immediately contact physician or poison control center. If conscious, rinse mouth with water. Do not give anything by mouth if person is unconscious or having convulsions.
- Inhalation: Move victim to fresh air. If not breathing, conduct artificial respiration; however, do not conduct mouth-to-mouth if victim has ingested or inhaled chemical. If breathing is difficult, administer oxygen. Seek immediate medical attention.
- Emergencies: 1-800-424-9300 or 703-527-3887.

References

Chem One. 2009. Material Safety Data Sheet: Potassium permanganate. Houston, TX. http://www.chemone.com/DEFAULT/MSDS/POTASSIUM%20PERMANGANATE.PDF. Accessed September 23, 2014.

Mackie, G. L. and R. Claudi. 2010. *Monitoring and control of macrofouling mollusks in fresh water systems, second edition*. Boca Raton, FL: CRC Press.

San Giacomo, R. and M. W. Wymer. 1997. Successful applications of zebra mussel treatment, excluding chlorine. In: *Zebra mussels and aquatic nuisance species*, ed.F. M. D'Itri, 501-506, Chelsea, MI: Ann Arbor Press.

4 Nonoxidizing Molluscicides

This group of chemicals includes most of the nongeneric and commercial formulations that have been registered for use in zebra mussel control. Their chemistry and activity differ from the oxidizing compounds, and they provide a different range of potential applications.

Quaternary and Polyquaternary Ammonium Compounds

These organic compounds comprise chemicals known as quaternary ammonium compounds (QACs) and polyquaternary ammonium compounds (poly-QACs or polyquats).

BULAB® 6002

Bulab® 6002 is a liquid cationic poly-QAC, a straight-chain ionene polymer with positively charged nitrogen atoms in the backbone of its polymeric chain (McMahon et al. 1993). It is used for algae control in swimming pools and as a microbiocide for the control of microorganisms in commercial and industrial water systems. It also is an effective molluscicide and can prevent biofouling by mollusks (Martin et al. 1993a; McMahon et al. 1993; Buckman Laboratories, Inc. 2009).

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: poly[oxyethylene(dimethyliminio)ethylene(dimethyliminio)ethylene dichloride
- Formulation: BULAB® 6002
    - 60 percent active ingredient
    - Liquid
- USEPA registration number 1448-42
- Source: Buckman Laboratories, Inc.
  1256 North McLean Boulevard
  Memphis, TN 38108
  1-800-282-5626

- Synonyms: BUSAN® 77, PQ1 (Buckman Laboratories, Inc. 2014)

Mode of Action

As a poly-QAC, Bulab® 6002 binds to negatively charged surfaces, including those of microorganisms and mollusk membranes.

Bulab® 6002 is not detected by zebra mussels as a noxious compound; therefore, valves remain open and siphons extended during the exposure period (McMahon et al. 1993).

Application Strategies

This product can be applied as a continuous or intermittent treatment. It can be applied with or without chlorine.

Timing of Application

This product is more effective at warmer water temperatures (Martin et al. 1993b).

Application Rates and Techniques

Recirculating or once-through industrial and cooling water systems: Apply at a rate of 2 to 20 mg L^{-1}. Intermittent or continuous additions can be made at the intake water. Continuous additions are needed for badly fouled systems and intermittent additions to maintain control.

Potable water systems: Apply at a rate of 2 to 5 mg L^{-1}. Continuous treatment for up to 21 days is used for badly fouled systems followed by regular control treatments. Control treatments are at a rate of 2 mg L^{-1} for 60 minutes, repeating daily; or 0.5 mg L^{-1} for continuous feed.

Contact a company representative for the most effective dosage for your system.

Maximum Water Concentrations

Concentrations of 2 to 5 mg L^{-1} can be used for up to 21 days; however, the long-term limit is 0.5 mg L^{-1} (Buckman Laboratories, Inc. 2009).

Use Restrictions

This product is toxic to fish, clams, and aquatic organisms.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority.

Timing of Results

Concentration and temperature effect timing of results (Martin et al. 1993a; Martin et al. 1993b).

Toxicological Data

Signal Word: Caution

Toxicity of Bulab® 6002 to aquatic species is listed in Table 8.

Table 8. Toxicity of Bulab® 6002[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	0.047 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	0.21 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50}	0.26 mg L^{-1}
Sheepshead Minnow (*Cyprinodon variegates*)	96 hr LC_{50}	≥600 mg L^{-1}
Mysid Shrimp (*Americamysis bahia*)	96 hr LC_{50}	13 mg L^{-1}

[1] From MSDS (Buckman Laboratories, Inc. 2011)

Precautions

- Harmful if swallowed or absorbed through skin.
- Avoid breathing vapors.
- Avoid contact with skin, eyes, and clothing.
- Causes moderate eye irritation.
- Wash thoroughly after handling.

Adjuvant/Detoxicant/Deactivant Use

None is needed.

Antidote Information

The following information is from the MSDS for Bulab® 6002 (Buckman Laboratories, Inc. 2011):

- Eyes: Immediately flush eyes with water for at least 15 minutes. Seek medical attention, preferably with an ophthalmologist.
- Skin or clothing: Wash with plenty of water. Remove contaminated clothing and wash before reuse. Seek medical attention if irritation persists.
- Ingestion: Do not induce vomiting. Irrigate esophagus and dilute stomach contents by slowly giving 1 or 2 glasses of water or milk. Do not give fluids by mouth if individual is comatose, semi-comatose, or convulsing. Seek medical attention.
- Inhalation: Immediately move exposed individual to fresh air. Seek immediate medical attention if individual experiences headache, dizziness, nausea, difficulty breathing, or is cyanotic.
- Emergencies: 901-767-2722

References

Buckman Laboratories, Inc. 2009. Bulab® 6002 information sheet. Memphis, TN. 1 p.

Buckman Laboratories, Inc. 2011. Material Safety Data Sheet: BULAB® 6002. Memphis, TN. 6 pp.

Buckman Laboratories, Inc. 2014. Master Label: BUSAN® 77. Memphis, TN. http://www.epa.gov/pesticides/chem_search/ppls/001448-00042-20140919.pdf. Accessed October 29, 2014.

Martin, I. D., G. L. Mackie, and M. A. Baker. 1993a. Control of the biofouling mollusk, *Dreissena polymorpha* (Bivalvia: Dreissenidae), with sodium hypochlorite and with polyquaternary ammonia and benzothiazole compounds. *Arch. Environ. Contam. Toxicol.* 24:381-388.

Martin, I. D., G. L. Mackie, and M. A. Baker. 1993b. Acute toxicity tests and pulsed-dose delayed mortality at 12 and 22 °C in the zebra mussel (*Dreissena polymorpha*). *Arch. Environ. Contam. Toxicol.* 24:389-398.

McMahon, R. F., B. N. Shipman, and D. P. Long. 1993. Laboratory efficacies of nonoxidizing molluscicides on the zebra mussel (*Dreissena polymorpha*) and the Asian clam (*Corbicula fluminea*). In: *Zebra mussels: Biology, impacts, and control*, ed. T. F. Nalepa and D. W. Schloesser, 575-598. Boca Raton, FL: Lewis Publishers.

BULAB® 6086

Bulab® 6086 is a liquid poly-QAC used for algae control in commercial and industrial recirculating cooling water towers and waste water systems. It is also used to control mollusks in once-through fresh and salt water cooling systems (Mason Chemical Company 2012).

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: Alkyl($_{C12-16}$)dimethylbenzyl ammonium chloride
- Formulation: BULAB 6086
    - 50 percent active ingredient
    - Liquid
- USEPA registration number 10324-42-1448
- Source: Buckman Laboratories, Inc.
  1256 North McLean Boulevard
  Memphis, TN 38108
  1-800-282-5626
- Synonyms: MAQUAT® MC1412-50%-W

Mode of Action

As a cationic surfactant, Bulab® 6086 binds to negatively charged surfaces, including those of microorganisms and mollusk membranes.

Application Strategies

It can be applied as an intermittent or continuous treatment.

n-alkyl dimethylbenzyl ammonium chloride is compatible with chlorine (Buecker and Post 1998).

Timing of Application

This product can be applied when the once-through cooling system is in jeopardy of being fouled or after cleaning systems where efficacy is already impaired.

Application Rates and Techniques

Apply this product at a point in the system where uniform mixing will occur, such as the sump.

Intermittent treatment: For the initial dose, apply at a rate of 0.154 to 1.54 fluid ounces per 1000 gallons of water based on system flow rates (0.6 to 6 ppm active quaternary basis) for 6 to 24 hours. Repeat until control is achieved. For subsequent doses, apply at a rate of 0.075 to 0.75 fluid ounces per 1000 gallons of water based on system flow rates (0.3 to 3 ppm active quaternary basis). Treat as needed to maintain control.

Continuous treatment: Apply at a rate of 0.25 to 2.575 fluid ounces per 1000 gallons (1 to 10 ppm active quaternary basis). Treatment time cannot exceed 120 hours per application.

Contact a company representative for the most effective dosage for your system.

Maximum Water Concentrations

Deactivation is required before discharge.

Use Restrictions

This product is toxic to fish, oysters, shrimp and aquatic invertebrates.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product into sewer systems without previously notifying the local sewage treatment plant authority.

It is prohibited to discharge effluent within ¼ mile of potable/drinking water intake.

Do not apply more than four times a year.

Timing of Results

Bulab® 6086 is fast acting.

Toxicological Data

Signal Word: Danger

No environmental toxicological information is listed on the MSDS (Buckman Laboratories, Inc. 2014).

n-alkyl dimethylbenzyl ammonium chloride has a favorable environmental profile and is readily biodegradable (Buecker and Post 1998).

Precautions

- Corrosive
- Harmful if absorbed through skin.
- Causes skin burns and irreversible eye damage.
- Avoid breathing vapors or spray mist.
- May be fatal if inhaled or swallowed.
- Avoid contact with skin, eyes and clothing.
- Wash thoroughly after handling.

Adjuvant/Detoxicant/Deactivant Use

To deactivate, use bentonite clay at a minimum ratio of 5 ppm clay:1 ppm product. Deactivation must occur prior to discharge.

Antidote Information

The following information is from the MSDS for Bulab® 6086 (Buckman Laboratories, Inc. 2014):

- Eyes: Immediately flush eyes with water for 15 to 20 minutes, removing contact lenses after the first 5 minutes. Seek medical attention.

- Skin or clothing: Wash with plenty of water for 15 to 20 minutes. Remove contaminated clothing and wash before reuse. Seek medical attention.
- Ingestion: Do not induce vomiting. If able, have person sip a glass of water. Do not give fluids by mouth if individual is comatose, semi-comatose, or convulsing. Seek immediate medical attention.
- Inhalation: Immediately move exposed individual to fresh air. Seek immediate medical attention. If individual is not breathing, call 911 and give artificial respiration.
- Emergencies: 901-767-2722

References

Buckman Laboratories, Inc. 2014. Material Safety Data Sheet: BULAB® 6086. Memphis, TN. 6 pp.

Buecker, B. and R. Post. 1998. Control biofouling in evaporative cooling systems. *Chem. Eng. Prog*. 94:45-50.

Mason Chemical Company. 2012. MAQUAT® MC1412-50%-W Master Label. http://www.epa.gov/pesticides/chem_search/ppls/010324-00042-20120322.pdf. Accessed October 29, 2014.

Clam-Trol CT-2

The primary active ingredient in Clam-Trol CT-2 is the cationic surfactant alkyl dimethylbenzyl ammonium chloride (ADBAC) (GE Betz, Inc. 2013). This product can be used to control mollusks in industrial water systems, once-through industrial cooling water systems, or auxiliary/service water and waste water systems.

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: Alkyl dimethylbenzyl ammonium chloride
- Formulation: Clam-Trol CT-2
    - 50 percent active ingredient
    - Liquid
- USEPA registration number 3876-149

- Source: GE Betz, Inc.
  4636 Somerton Road
  Trevose, PA 19053
  215-355-3300

- Synonyms: Spectrus CT1300

Mode of Action

This product is a surfactant that destroys mollusk branchiae (Rajagopal et al. 2012).

Application Strategies

This product can be applied as a slug dose, continuous feed, or intermittent application.

Timing of Application

This product can be applied as needed. See Application Rates and Techniques section for timing information on specific applications.

Application Rates and Techniques

Badly fouled systems must be cleaned before treating with this product.

Industrial water treatment: Apply at a rate of 0.016 to 0.166 pounds (2 to 20 ppm) per 1000 gallons of water. Maintain concentration for 3 to 96 hours.

Once-through industrial cooling water systems:

- Slug dose: Apply at a rate of 0.008 to 0.160 pounds per 1000 gallons of water (1 to 20 ppm) based on flow rate. Maintain concentration for 1 to 96 hours.
- Continuous feed: Add at a rate of 0.002 to 0.024 pounds per 1000 gallons of water (0.25 to 3 ppm) based on flow rate. Apply when zebra mussels are spawning. Repeat application during the following year's spawning season.
- Intermittent application: Apply at a rate of 0.004 to 0.08 pounds per 1000 gallons of water (0.5 to 10 ppm) for 30 minutes to 6 hours daily

during the spawning season. Repeat application during the following year's spawning season.

Auxiliary water/service water and waste water systems: Treat as needed. Apply at a rate of 0.3 to 1.3 pounds per 1000 gallons of water (36 to 156 ppm) already in the system or being added to the system, for 4 to 8 hours, 1 to 4 times per week. After control is obtained, apply at a rate of 0.15 to 0.65 pounds per 1000 gallons of water (18 to 78 ppm) every 3 days or as needed to maintain control.

Maximum Water Concentrations

This product must be deactivated prior to discharge unless the NPDES permit for the facility does not require it.

Use Restrictions

This product is toxic to fish.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority.

Do not use water containing residues of this product to irrigate food or feed crops.

Do not use this product in potable/drinking water systems.

Use of this product in cooling water systems that discharge within ¼ mile of potable/drinking water intakes is strictly prohibited.

Timing of Results

Treatment effects occur within a few days.

Toxicological Data

Signal Word: Danger

Toxicity of Clam-Trol CT-2 to aquatic species is listed in Table 9.

Table 9. Toxicity of Clam-Trol CT-2[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50} flow-thru	2.00 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50} flow-thru	0.72 mg L^{-1}
Channel Catfish (*Ictalurus punctatus*)	96 hr LC_{50}	0.86 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	0.11 mg L^{-1}
Freshwater Snail (*Physa sp.*)	96 hr LC_{50}	0.46 mg L^{-1}
Midge Larvae (*Chironomus tentans*)	96 hr LC_{50}	0.50 mg L^{-1}
Annelida (*Lumbriculus variegatus*)	96 hr LC_{50}	1.47 mg L^{-1}

[1] From MSDS (GE Betz, Inc. 2014)

Precautions

- Corrosive.
- Do not get in eyes, on skin, or on clothing.
- May be fatal if swallowed, absorbed through skin, or inhaled.
- Do not breathe spray mist.
- Causes irreversible eye damage and skin burns.
- Wash thoroughly after handling.
- Wash contaminated clothing before reuse.

Adjuvant/Detoxicant/Deactivant Use

To deactivate, use bentonite clay at a minimum ratio of 5 ppm clay:1 ppm product. Deactivation must occur prior to discharge.

Antidote Information

The following information is from the MSDS for Clam-Trol CT-2 (GE Betz, Inc. 2014):

- Eyes: With eyelids open, immediately flush eyes with water for at least 30 minutes. Remove contact lenses. Seek medical attention.
- Skin or clothing: Wash thoroughly with soap and water. Remove contaminated clothing. Wash clothing before reuse. Seek immediate medical attention.

- Ingestion: Rinse mouth with water. Do not give anything to drink or eat. Do not induce vomiting. Do not give anything by mouth to an unconscious or convulsing person. Seek immediate medical attention.
- Inhalation: Move person to fresh air. Give oxygen if breathing is difficult. Give artificial respiration if breathing has stopped. Seek immediate medical attention.
- Emergencies: 1-800-877-1940

References

GE Betz, Inc. 2013. Master Label: Clam-Trol CT-2. Trevose, PA. http://www.epa.gov/pesticides/chem_search/ppls/003876-00149-20130709.pdf. Accessed August 21, 2014.

GE Betz, Inc. 2014. Material Safety Data Sheet: SPECTRUS CT1300. Trevose, PA. http://www.gewater.com/msds-material-data-safety-sheets.html#. Accessed September 12, 2014.

Rajagopal, S. R., H. A. Jenner, V. P. Venugopalan and M. Khalanski. 2012. Biofouling control: alternatives to chlorine. In: *Operational and environmental consequences of large industrial cooling water systems*, ed. S. Rajagopal, H. A. Jenner, and V. P. Venugopalan, 227-271. New York, NY: Springer.

H-130 Microbiocide

H-130 Microbiocide is a nonoxidizing molluscicide, which is effective against zebra mussel adults, juveniles, and veligers in once-through cooling water systems. It does not form corrosive by-products and therefore does not accelerate corrosion of metal surfaces (Nalco Company 2013).

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: H-130 Microbiocide
- Formulation: didecyl dimethyl ammonium chloride
    - 50 percent active ingredient
    - Liquid
- USEPA registration number 1706-186
- Source: Nalco Company
  1601 West Diehl Road
  Naperville, IL 60563-1198
  1-630-305-1000

- Synonyms: DDAC

Mode of Action

This product is a surfactant that destroys mollusk branchiae (Rajagopal et al. 2012).

Application Strategies

Slug feed for once-through systems.

Timing of Application

Apply periodically to limit accumulation of adults, but no more than four times per year.

Application Rates and Techniques

Product must be applied using a metering pump directly from pail or drum.

Add product at a point where it will be uniformly mixed and distributed.

Slug dose: Apply at a rate of 0.15 to 1.5 ounces per 1000 gallons of water (1 to 10 ppm as product). Do not exceed 120 hours per application. Do not apply more than four times per year.

Maximum Water Concentrations

This product must be deactivated prior to discharge unless the NPDES permit for the facility does not require it.

Use Restrictions

This product is toxic to fish, oysters, shrimp, and aquatic invertebrates.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority.

Do not use treated water for irrigating food or feed crops.

Do not use this product in potable/drinking water systems.

Use of this product in cooling water systems that discharge within ¼ mile of potable/drinking water intakes is strictly prohibited.

Do not exceed 120 hours per application.

Do not apply more than four times per year.

Timing of Results

Results are usually seen within 24 hours of treatment program start.

Toxicological Data

Signal Word: Danger

Toxicity of H-130 Microbiocide to aquatic species is presented in Table 10.

Table 10. Toxicity of H-130 Microbiocide[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	1.0 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	0.32 mg L^{-1}
Coho Salmon (*Oncorhynchus kisutch*)	96 hr LC_{50}	1.0 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50}	0.19 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	0.19 mg L^{-1}

[1] From MSDS (Nalco Company 2011)

Precautions

- Corrosive.
- Avoid contact to eyes, skin, and clothing.
- Causes irreversible eye damage and skin burns.
- Do not breathe spray mist or vapor.
- Wash thoroughly after handling.

- Wash contaminated clothing before reuse.

Adjuvant/Detoxicant/Deactivant Use

Use bentonite clay at a minimum ratio of 5 ppm clay:1 ppm product. Deactivate prior to discharge.

Antidote Information

The following information is from the MSDS for H-130 Microbiocide (Nalco Company 2013):

- Eyes: With eyelids open, rinse gently with water for 15 to 20 minutes. Remove contact lenses after the first 5 minutes. Seek medical attention.
- Skin or clothing: Remove contaminated clothing. Rinse skin with water for 15 to 20 minutes. Seek medical attention.
- Ingestion: Call poison control center or doctor for treatment advice. If able to swallow, have individual sip water. Do not induce vomiting unless told to do so by poison control center or doctor. Do not give anything by mouth to an unconscious person.
- Inhalation: Move person to fresh air. If not breathing, call 911 and give artificial respiration. Seek medical attention.
- Emergencies: 1-800-424-9300.

References

Nalco Company. 2011. Material Safety Data Sheet: H-130 Microbiocide. Naperville, IL. 11 pp.

Nalco Company. 2013. Master Label H-130 Microbiocide. Naperville, IL. http://www.epa.gov/pesticides/chem_search/ppls/001706-00186-20131022.pdf. Accessed August 22, 2014.

Rajagopal, S. R., H. A. Jenner, V. P. Venugopalan and M. Khalanski. 2012. Biofouling control: alternatives to chlorine. In: *Operational and Environmental Consequences of Large Industrial Cooling Water Systems*. S. Rajagopal, H. A. Jenner, and V. P. Venugopalan eds., Springer, New York, NY, 227-271.

Slimicide™ C-74

Slimicide™ C-74 is a mixture of alkyl dimethylbenzyl ammonium chloride (ADBAC) and dodecylguanidine hydrochloride (DGH) (GE Betz, Inc. 2010). This product can be used to control mollusks in recirculating cooling water systems, once-through industrial cooling water systems, auxiliary water systems, and wastewater systems.

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: Alkyl dimethylbenzyl ammonium chloride (ADBAC) + dodecylguanidine hydrochloride (DGH)
- Formulation: Slimicide™ C-74
    - 8 percent ADBAC + 5 percent DGH
    - Liquid
- USEPA registration number 3876-145
- Source: GE Betz, Inc.
  4636 Somerton Road
  Trevose, PA 19053
  215-355-3300

Mode of Action

The QAC compounds destroy the branchiae of mollusks (Rajagopal et al. 2012).

Application Strategies

This product can be applied as a continuous feed or as an intermittent or slug feed.

Timing of Application

This product can be applied when the system is noticeably fouled.

Application Rates and Techniques

Badly fouled systems must be cleaned before using this product.

Recirculating cooling water systems:

- Intermittent or slug method: Apply an initial dose of 0.3 to 2.0 pounds per 1000 gallons of water in the system (36 to 240 ppm). Repeat until control is achieved. Subsequent doses should be applied at a rate of 0.15 to 1.5 pounds per 1000 gallons of water (18 to 180 ppm) every three days or as needed to maintain control.

- Continuous feed method: Apply at an initial rate of 0.3 to 2.0 pounds per 1000 gallons of water in the system (36 to 240 ppm). Subsequent dose should be continuously fed at a rate of 0.05 to 0.5 pounds per 1000 gallons of water in the system (6 to 60 ppm).

Once-through industrial cooling water systems:

- This product should be added via a metering pump.
- Intermittent or slug method: Apply an initial dose of 0.2 to 1.0 pounds per 1000 gallons of water (24 to 120 ppm) based on flow rate. Repeat until control is achieved. Minimum treatment intervals should be 15 minutes. Subsequent doses should be applied at a rate of 0.05 to 0.5 pounds per 1000 gallons of water (6 to 60 ppm) intermittently as needed to maintain control.
- Continuous feed method: Apply at an initial rate of 0.2 to 1.0 pounds per 1000 gallons of water (24 to 120 ppm) based on flow rate. Continue until control is achieved. Subsequent dose should be continuously fed at a rate of 0.02 to 0.2 pounds per 1000 gallons of water based on flow rate (2.4 to 24 ppm).

Auxiliary water systems:

- Non-potable systems only
- Intermittent or slug method: Apply at a rate of 1.5 to 4.0 pounds per 1000 gallons of water in the system or being added to the system for 4 to 8 hours, 1 to 4 times per week, or as needed to achieve control. Once control is obtained, apply at a rate of 0.75 to 2.0 pounds per 1000 gallons of water in the system.

Wastewater systems:

- Add product during the pumping operation or as close to the pump as possible to ensure adequate mixing.
- Intermittent or slug method: Apply at a rate of 1.5 to 4.0 pounds per 1000 gallons of water in the system or being added to the system for 4 to 8 hours, 1 to 4 times per week or as needed to achieve control. Once control is obtained, apply at a rate of 0.75 to 2.0 pounds per 1000 gallons of water in the system.

Maximum Water Concentrations

The maximum water concentration is designated in an NPDES permit for an individual facility.

Use Restrictions

This product is toxic to fish and wildlife.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority.

Timing of Results

Treatment effects occur within a few days.

Toxicological Data

Signal Word: Danger

Toxicity of Slimicide™ C-74 to aquatic species is presented in Table 11.

Table 11. Toxicity of Slimicide™ C-74[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50} flow-thru	8.1 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50} flow-thru	2.9 mg L^{-1}
Sheepshead Minnow (*Cyprinodon variegates*)	96 hr LC_{50} static	7.0 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50} flow-thru	0.2 mg L^{-1}
Mysid Shrimp (*Americamysis bahia*)	96 hr LC_{50} flow-thru	0.34 mg L^{-1}

[1] From MSDS (GE Betz, Inc. 2011)

Precautions

- Corrosive.
- Do not get in eyes, on skin, or on clothing.
- May be fatal if swallowed, absorbed through skin, or inhaled.

- Avoid breathing spray mist or vapor.
- Causes irreversible eye damage and skin burns.
- Wash thoroughly after handling.
- Wash contaminated clothing before reuse.

Adjuvant/Detoxicant/Deactivant Use

None is specified on the label; however, QAC compounds can be deactivated using bentonite clay at a minimum ratio of 5 ppm clay:1 ppm product.

Antidote Information

The following information is from the MSDS for Slimicide™ C-74 (GE Betz, Inc. 2011):

- Eyes: With eyelids open, immediately flush eyes with water for at least 20 minutes. Remove contact lenses. Seek immediate medical attention.
- Skin or clothing: Wash thoroughly with soap and water. Remove contaminated clothing. Wash clothing before reuse. Seek immediate medical attention.
- Ingestion: Do not induce vomiting. Do not give anything by mouth to an unconscious or convulsing person. Dilute stomach contents with 2 to 8 ounces of milk or water. Seek immediate medical attention.
- Inhalation: Move person to fresh air. Give oxygen if breathing is difficult. Give artificial respiration if breathing has stopped. Seek immediate medical attention.
- Emergencies: 1-800-877-1940

References

GE Betz, Inc. 2010. Master Label: Slimicide C-74. Trevose, PA. http://www.epa.gov/pesticides/chem_search/ppls/003876-00145-20100722.pdf. Accessed August 21, 2014.

GE Betz, Inc. 2011. Material Safety Data Sheet: Slimicide C-74. Trevose, PA. http://www.gewater.com/msds-material-data-safety-sheets.html#. Accessed September 12, 2014.

Rajagopal, S. R., H. A. Jenner, V. P. Venugopalan and M. Khalanski. 2012. Biofouling control: alternatives to chlorine. In: *Operational and environmental consequences of large industrial cooling water systems*, ed. S. Rajagopal, H. A. Jenner, and V. P. Venugopalan, 227-271. New York, NY: Springer.

VeliGON

VeliGON TL-M is used to control mollusks in water supplies (Nalco Company 2013).

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: poly (dimethyldiallyl ammonium chloride)
- Formulation: VeliGON™ TL-M
    - 19.8 percent
    - Liquid
- USEPA registration number 1706-226
- Source: Nalco Company
  1601 West Diehl Road
  Naperville, IL 60563-1198
  630-305-1000

Mode of Action

The mechanisms of toxicity and uptake of poly(dimethyldiallyl ammonium chloride) by zebra mussels is not fully understood (Costa et al. 2008).

Application Strategies

Apply as a continuous feed.

Timing of Application

Apply during the breeding season when veligers are present in intake water.

Application Rates and Techniques

Add product to system at a rate of 0.6 fluid ounces per 1000 gallons of intake water. Apply at a point sufficiently inside the intake pipe to prevent release of this product into the intake source. The supply line should be placed inside the intake pipe to ensure no contamination of public waters could occur in the event of a break. Feed exits must have a pressure check

valve at the feed line exit to seal the feed line when intake flows stop. Feed pumps must be stopped half an hour prior to planned shut downs.

Maximum Water Concentrations

Limit residues of poly (dimethyldiallyl ammonium chloride) in finished potable water to no more than 50 ppb (0.05 ppm).

Use Restrictions

This product is toxic to aquatic vertebrates and fish.

Do not use in facilities discharging indirectly or directly to marine or estuarine environments.

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority.

Timing of Results

Significant treatment effects on individuals are seen within three days.

Toxicological Data

Signal Word: Caution

Toxicity of VeliGON™ TL-M to aquatic species is listed in Table 12.

Table 12. Toxicity of VeliGON™ TL-M[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	0.74 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	1.8 mg L^{-1}

[1] From MSDS (Nalco Company 2014)

Precautions

- Avoid contact with skin, eyes, and clothing.

Adjuvant/Detoxicant/Deactivant Use

None is specified.

Antidote Information

The following information is from the MSDS for VeliGON™ TL-M (Nalco Company 2014):

- Eyes: Rinse with plenty of water. If symptoms occur, get medical attention.
- Skin or clothing: Wash with soap and water. If symptoms occur, get medical attention.
- Ingestion: Rinse mouth. If symptoms occur, get medical attention.
- Inhalation: If symptoms occur, get medical attention.
- Emergencies: 1-800-424-9300

References

Costa, R., D. C. Aldridge, and G. D. Moggridge. 2008. Seasonal variation of zebra mussel susceptibility to molluscicidal agents. *J. Appl. Ecol.* 45(6):1712-1721.

Nalco Company. 2013. Master label: VeliGON TL-M. Naperville, IL. http://www.epa.gov/pesticides/chem_search/ppls/001706-00226-20130226.pdf. Accessed August 22, 2014.

Nalco Company. 2014. Material Safety Data Sheet: VeliGON™ TL-M. Naperville, IL. 8 pp.

Aromatic Hydrocarbons

These compounds are ring-structure organics with film-forming and surfactant activity and include formulations that have been used as biocides in industrial water-handling systems for many years.

MEXEL® 432/0

This patented emulsion of alkylamines uses surface-active properties to inhibit sources of water circuit fouling in fresh and salt water, including macrofouling from mollusks, crustaceans, barnacles, and hydroids. Mexel® 432/0 adsorbs to all exposed surfaces of any material type to form a protective film on internal components that remain in place until it

degrades. The aliphatic nature of the amine surfactant film also protects surfaces from corrosion (including MIC and crevice), and acts as a scale and mud dispersant (Giamberini et al. 1994; Armon et al. 2008; Lopez-Galindo et al. 2010).

Chemical Name and Formulations

This product has the following characteristics:

- Chemical name: 1-(Alkyl*amino)-3-aminopropane
  *as in fatty acids of coconut oil
- Formulation: Mexel® 432/0
  - 1.7 percent active ingredient
  - Liquid
- USEPA Registration No. 84034-1
- U.S. Distributor: Mexel USA, LLC
  1655 N. Fort Myer Dr. #350
  Arlington, VA 22209
  703-349-3347

Mode of Action

This hydrocarbon compound is a mixture of aliphatic hydrocarbons, with alcohol and amine functionality, in an aqueous emulsion. The aliphatic amines act as surfactants, or "filming amines," and adhere to wetted metal, plastic, concrete, and glass surfaces to form a protective film. The product inhibits the definitive settlement of mussels by retarding byssal thread formation (Giamberini et al. 1995), limiting adherence to surfaces, and gradually killing zebra mussels already in place by damaging gill surface membranes (Czembor et al. 1997), and dispersing mussels. Thus, it prevents new infestations and gradually disperses existing infestations. It is most effective when used to prevent infestations in a previously cleaned system.

Application Strategies

Mexel® 432/0 is used to control mollusks, including zebra mussels, in non-potable industrial water systems (Mexel USA, LLC 2014a). It may be applied to maintain clean systems or to treat systems that are already

fouled. For best results, the system should first be cleaned of adult zebra mussels and then treated.

Treatment is usually on an intermittent basis or as needed to maintain control. Intermittent injection of lower concentrations has been shown to have the potential for reducing molluscicide quantities while maintaining effectiveness (Giamberini et al. 1994). Automated injection is possible at a variety of locations in the water system.

Mexel® 432/0 can be employed in recirculating water systems as well as in open, once-through cooling systems. It is also effective as an acute toxicant for systems that do not have continuous water flow (i.e., fire protection systems, standby facilities) and when discharge is treated (Renaud et al. 2010).

Timing of Application

Initial application early in the season prior to veliger settlement, with continuation of daily dosing throughout the growing season.

Application Rates and Techniques

Dosage is a function of the volume of water in the system. For once-through systems, volume equals the total flow over the 30-minute daily treatment period. In recirculating systems, dosage is calculated on the total water volume in the system.

A standard treatment is 4 to 5 ppm for 20 to 30 minutes per day to achieve a residual level in the water of 2.5 ppm. Monitor the presence of Mexel® 432/0 with colorimetric tests of grab samples. Less frequent dosing and lower residual levels may be possible in certain situations.

Maximum Water Concentrations

Maximum potential concentration in discharged water is 2.5 ppm. Actual levels in discharges are typically much lower due to a number of factors, including immediate demand due to film adhering to surfaces and materials in the water (i.e., suspended solids), water circuit configuration, and other factors.

Use Restrictions

This product is toxic to fish, oysters, shrimp, and aquatic invertebrates.

Do not discharge into lakes, ponds, streams, estuaries, oceans, or other surface waters unless in accordance with a NPDES permit. For guidance, contact your state water board or a regional office of the USEPA.

Do not contaminate water, food, or feed by storage or disposal.

Timing of Results

Treatment shows effects within a few weeks, but continued treatment is required. Monitor treatment efficacy with visual inspections, biofilm coupons, corrosion coupons, etc., at appropriate points in the system.

Toxicological Data

Signal Word: Danger

Note: Standard testing has organisms continuously exposed for long periods of time; however, Mexel® 432/0 is only dosed for 30 minutes per day. This intermittent dosing at sublethal concentrations means that only organisms that remain within the treated system are at risk. Tables 13 and 14 summarize the aquatic toxicology for Mexel® 432/0 for static and acute tests, respectively.

Table 13. Toxicity of Mexel® 432/0 under continuous (static) exposures[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss)*	96 hr LC_{50}	0.73 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	0.55 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50}	0.36 mg L^{-1}

[1] From Ghillebaert 2012

Table 14. Toxicity of Mexel® 432/0 under short daily exposures[1,2] to aquatic species.

Organism	Daily Exposure	LC_{50} Result
Water Flea (*Daphnia magna*)	5 min	26.9 mg L^{-1}
	20 min	6.3 mg L^{-1}
	80 min	3.0 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	5 min	13.1 mg L^{-1}
	20 min	6.2 mg L^{-1}
	80 min	2.2 mg L^{-1}

[1] From Ghillebaert 2012, [2] 96 hr observation period

Precautions

- Corrosive.
- Can cause severe eye irritation.
- Harmful if swallowed, inhaled, or absorbed through skin.
- Wash thoroughly after handling.

Adjuvant/Detoxicant/Deactivant Use

No detoxification is required.

Antidote Information

The following information is from the MSDS for Mexel ® 432/0 (Mexel 2014b):

- Eyes: Immediately move individual away from exposure and into fresh air. Gently flush eyes with water for at least 15 minutes while holding eyelids apart. Seek immediate medical attention.
- Skin or clothing: Remove contaminated clothing. Wash exposed area with soap and water. Flush skin with water for at least 15 minutes. If symptoms persist, seek medical attention. Wash clothing before reuse.
- Ingestion: Seek medical attention. Do not give anything by mouth if individual is drowsy or unconscious. Place individual on left side with head down. Do not induce vomiting. Contact a physician, medical facility, or poison control center. If possible, do not leave individual unattended.
- Inhalation: Move individual away from exposure and into fresh air. If symptoms persist, seek medical attention. If breathing is difficult, administer oxygen.
- Emergencies: 1-800-424-9300

References

Armon, T., D. Barkauskas, J. J. Cohen, E. C. Mallen. 2008. Mexel efficiency study. HOH Report. http://pbadupws.nrc.gov/docs/ML0913/ML091340525.pdf.

Czemobr, N., L. Giamberini, and J. C. Pihan. 1997. Effects of MEXEL 432 on pumping and valve activities of zebra mussel: used of a new experimental evaluation system. *Proceedings of the Seventh International Zebra Mussel Conference, New Orleans, LA, January 28-31, 1997.*

Ghillebaert, F. 2012. Untitled presentation summarizing environmental characteristics of Mexel products. Prepared for Mexel Industries SAS, Verberie, France.

Giamberini, L., N. Czembor, and J. C. Pihan. 1995. Inhibitory effects of an organic molluscicide on byssal thread development in zebra mussels. *J. Invertebr. Pathol. 66:205-206.*

Giamberini, L., N. Czembor, and J. C. Pihan. 1994. Effects of MEXEL 432 on the settling, detachment and mortality of adult zebra mussels. *Proceedings of the Fourth International Zebra Mussel Conference, Madison, WI, March 7-10, 1994.*

Lopez-Galindo, C., J. F. Casanueva, and E. Nebot. 2010. Efficacy of different antifouling treatments for seawater cooling systems. *Biofouling* 26(8):923-930.

Mexel USA, LLC. 2014a. Mexel® 432/0 label. Arlington, VA. 1 pg.

Mexel USA, LLC. 2014b. Mexel® 432/0 Material Safety Data Sheet. Arlington, VA. 10 pp.

Renaud, C., C. de Grandmaison, and F. Ghillebaert. 2010. Mexel® 432: Environmentally friendly protection and treatment of cooling water circuit. In: POWER-GEN Middle East. Qatar. 16 pp.

Endothall

The amine salt of the compound endothall has been used as an herbicide (HYDROTHOL 191) against submersed weeds in aquatic environments for a number of years, and its effects on aquatic systems are well understood. It has been found to be effective against zebra mussels, and a formulation has been registered as EVAC™ for molluscicidal use.

EVAC™

Chemical Name and Formulations

This formulation has the following characteristics:

- Chemical name: mono (N,N-dimethylalkylamine) salt of endothall
- Formulation: EVAC™

  - 53.0 percent active ingredient
  - Liquid

- USEPA registration number 70506-189
- Source: Nalco Company
  W. Diehl Rd
  Naperville, IL 60563-1198
  1-630-305-1000

- Synonym: TD 2335 (United Phosphorus, Inc. 2010)

Mode of Action

Mussels do not sense this compound in the water and therefore do not close their shells; continued siphoning brings the material into contact with tissues where it acts as a corrosive to membranes, including gills.

Application Strategies

EVAC™ can be used to control established mollusk populations as well as prevent settlement of veligers.

Timing of Application

Use when established populations are present.

During the breeding season, it can be used to prevent settlement of veligers.

Application Rates and Techniques

Toxicity is dependent on concentration and exposure time.

This product can be metered directly into the system.

For established populations in recirculating and once-through cooling water systems, apply at a rate of 0.3 to 3.0 ppm endothall technical for 6 to 144 hours of exposure.

Higher rates and longer exposures are required for heavy mollusk populations and/or when water temperatures are less than 70 °F (21 °C).

Maximum Water Concentrations

The MCL for endothall in drinking water is 0.1 mg L^{-1} (USEPA 2009).

Use Restrictions

EVAC™ is toxic to fish. Do not discharge effluent containing EVAC into streams, lakes, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit. Prior to discharge, the permitting authority must be notified in writing.

Do not discharge effluent containing EVAC™ into sewage systems without prior notification to the local sewage treatment authority.

Timing of Results

Treatment effects are evident within a few days of treatment.

Toxicological Data

Signal Word: Danger

Toxicity data for EVAC™ to aquatic species is shown in Table 15.

Table 15. Toxicity of EVAC™[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	0.29 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	0.50 mg L^{-1}
Fathead Minnow (*Pimephales promelas*)	96 hr LC_{50}	0.25 mg L^{-1}
Water Flea (*Daphnia magna*)	48 hr LC_{50}	0.09 mg L^{-1}
Crayfish (species not specified)	96 hr LC_{50}	1.96 mg L^{-1}
Midges (*Diptera*)	96 hr LC_{50}	0.64 mg L^{-1}

[1] From MSDS (Nalco Company 2011)

Precautions

- Corrosive. Causes irreversible eye damage and skin burns
- May be fatal if absorbed through skin or swallowed.
- Harmful if inhaled.
- Do not get on skin, clothing, or in eyes.
- Do not ingest.

- Do not breathe spray mist or vapor.
- Wash thoroughly after handling.

Adjuvant/Detoxicant/Deactivant Use

EVAC™ does not require deactivation or a holding period. Product rapidly dissipates in water.

Antidote Information

The following information is from the MSDS for EVAC (Nalco Company 2011):

- Eyes: Holding eyelids open, slowly and gently rinse with water for 15 to 20 minutes. If wearing contact lenses, remove lenses after five minutes of rinsing and continue to rinse. Call doctor or poison control center for treatment advice.
- Skin or clothing: Remove contaminated clothing. Immediately rinse skin with plenty of water for 15 to 20 minutes. Call doctor or poison control center for treatment advice.
- Ingestion: Call doctor or poison control center for treatment advice. If able to swallow, sip a glass of water. Do not induce vomiting unless told to by a doctor or poison control center.
- Inhalation: Move person to fresh air. If not breathing, call 911, then give artificial respiration. Call doctor or poison control center for treatment advice.
- Emergencies: 1-800-424-9300

References

Nalco Company. 2011. EVAC Biocide Material Safety Data Sheet. Naperville, IL. 11 pp.

United Phosphorus, Inc. 2010. TD2335 Industrial Biocide-Molluscicide label. King of Prussia, PA. 4 pp.

USEPA. 2009. The national primary drinking water regulations. http://www.epa.gov/safewater/consumer/pdf/mcl.pdf. Accessed May 30, 2014.

Metals and Their Salts

Both copper and a range of potassium salts have been shown to have activity against zebra mussels. Their low toxicity to other organisms in water and long history of use in water treatment make them potential solutions for a range of problem zebra mussel sites and systems.

Copper Ions

The presence of excess copper ions in water is inimical to a number of aquatic organisms, including algae, plants, mussels, and clams, and has a long history of use in marine antifouling coatings. Kennedy et al. (2006) determined that the early life stages of zebra mussels are significantly more susceptible than adults to copper applied as either Cutrine-Ultra®* (Applied Biochemists, Germantown, WI) or copper sulfate ($CuSO_4$). Based on analysis, they estimate that 200 µg Cu L^{-1} for 24 hours or 400 µg Cu L^{-1} for 3 hours would kill 99 percent of zebra mussel larvae, whereas it would take 2000 µg Cu L^{-1} for 96 hours to kill a similar percent of adult mussels. The difference in sensitivity is due to the ability of adult zebra mussels to detect copper and close their shells and adults are more resistant to copper toxicity (Kennedy et al. 2006). Although early zebra mussel life stages are more sensitive to copper than adults, copper has still been reported to be highly toxic to adults (Rao and Khan 2000). Rao and Khan (2000) report that temperature plays a significant role in copper toxicity; for example, the 48 hour LC_{50} for copper at 25 and 20 °C is 238 µg L^{-1} and 775 µg L^{-1}, respectively.

Copper ion technology (MacroTech®) is also used to control zebra mussels. This technology involves copper and aluminum anodes to supply copper ions to the water and will be discussed later in this section (Mackie and Claudi 2010).

*Cutrine-Ultra is not currently registered for control of zebra mussels.

References

Kennedy, A. J., R. N. Millward, J. A. Steevens, J. W. Lynn, and K. D. Perry. 2006. Relative sensitivity of zebra mussel (*Dreissena polymorpha*) life stages to tow copper sources. *J. Great. Lakes Res.* 32:596-606.

Mackie, G. L. and R. Claudi. 2010. *Monitoring and control of macrofouling mollusks in fresh water systems, second edition*. Boca Raton, FL: CRC Press.

Rao, D. G. V. P. and M. A. Q. Khan. 2000. Zebra mussels: Enhancement of copper toxicity by high temperature and its relationship with respiration and metabolism. *Water Environ. Res.* 72(2):175-178.

Natrix™

Natrix™ is an aquatic pesticide approved to control zebra and quagga mussels. Unlike other products listed in this control guide, Natrix™ can be

applied to natural or manmade surface waters (i.e., open water systems). At the time of this publication, states with FIFRA 24(C) Special Local Needs (SNL) labels include Georgia, Idaho, Missouri, South Carolina, and Texas (SePRO Corporation 2010a, b, c and 2011a, b). For current information on states with approved SLN labels or application rates and exposures, contact SePRO Corporation.

Chemical Name and Formulations

- Chemical name: copper carbonate
- Formulation: Natrix™
    - 15.9 percent active ingredient
    - Liquid
- USEPA registration number 67690-9
- Source: SePRO Corporation
  11550 North Meridian St.
  Suite 600
  Carmel, IN 46032
  1-800-419-7779

Mode of Action

Natrix™ disrupts osmoregulation causing oxidative stress to both zebra mussel veligers and adults.

Application Strategies

Natrix™ is effective under both high-rate short exposure and low-rate long exposure scenarios (SePRO Corporation 2014). It can be used to prevent zebra mussels from settling and establishing and can also be used to control adult mussels.

Timing of Application

Timing of applications is dependent on site-specific objectives and level of infestation. There are no timing restrictions.

Application Rates and Techniques

Rates and exposure times can vary, depending on treatment conditions and life stage. Use the lowest rate and frequency necessary. Below are general guidelines.

In flowing water, maintain injection rate for a minimum of 24 hours.

In potable water with an active water intake, treat at a rate of 3 gallons per acre-foot in static water or 32 ounces per cubic feet per second (cfs) per hour in flowing water.

In non-potable water or in potable water with intakes that can be turned off, treat at a rate up to 7.4 gallons per acre-foot in static water. In flowing water, treat at a rate up to 78.9 ounces per cfs per hour. Water intakes can be turned back on when copper concentrations are less than 1 ppm at the intake.

Repeat applications may be necessary for adult zebra mussels and certain site conditions.

Maximum Water Concentrations

The maximum concentration of Natrix™ in potable water is 1 ppm and 2.5 ppm in non-potable water.

Use Restrictions

Do not treat more than half of the waterbody at one time to avoid oxygen depletion.

Only for use by federal, state, or other government agencies or by certified aquatic pest control applicators certified by state or local government.

Do not turn potable water intakes on until copper concentration is less than 1 ppm at the intake.

Timing of Results

Depending on the life stage of zebra mussels being controlled and the concentration and exposure time of Natrix™, results can be seen in hours to less than five days.

Toxicological Data

Signal Word: Danger

Toxicity data for Natrix™ to aquatic species is shown in Table 16.

Table 16. Toxicity of Natrix™ Proprietary Amines[1] to aquatic species.

Organism	Test	Result
Proprietary Amine		
Shrimp (*Crangon crangon*) Adult	48 hr LC_{50}	>100 mg L^{-1}
Fathead Minnow (*Pimephales promelas*) 30 day	96 hr LC_{50}	11800 mg L^{-1}
Daphnia (*Daphnia magna*) ≤1 day	21 day NOEC	16 mg L^{-1}
Proprietary Amine 2		
Algae (*Isochrysis galbana*)	96 hr EC_{50}	80 mg L^{-1}
Shrimp (*Crangon crangon*) Adult	48 hr LC_{50}	>100 mg L^{-1}
Rainbow Trout (*Oncorhynchus mykiss*) Yolk-Sac Fry	96 hr LC_{50}	150 mg L^{-1}

[1] From MSDS (SePRO Corporation 2012)

Precautions

- Do not get on skin or clothing or in eyes.
- Do not ingest.
- Do not breathe mist or vapor. Only use with adequate ventilation.
- Wash thoroughly after handling.

Adjuvant/Detoxicant/Deactivant Use

No adjuvant, detoxicant, or deactivant is required with use of Natrix™.

Antidote Information

The following information is from the MSDS for Natrix™ (SePRO Corporation 2012):

- Eyes: Remove contact lenses. Immediately flush eyes for at least 20 minutes with plenty of water. Occasionally lift upper and lower eyelids. Get immediate medical attention.
- Skin or clothing: Remove contaminated shoes and clothing. Immediately flush skin with plenty of water for at least 20 minutes.

Wash shoes and clothing before reuse. Get immediate medical attention.

- Ingestion: Wash mouth out with water. Do not induce vomiting unless directed to do so by medical personnel. If unconscious, do not give anything by mouth. Get immediate medical attention.
- Inhalation: Move to fresh air. Provide artificial respiration or oxygen if not breathing or breathing is irregular. Loosen tight-fitting clothing. Get immediate medical attention.
- Emergencies: 1-800-535-5053

References

SePRO Corporation. 2010a. Natrix™ – Special Local Need (SLN) Label (FIFRA 24(c).). EPA SLN No. MO-100005. 1 pp.

SePRO Corporation. 2010b. Natrix™ – Special Local Need (SLN) Label (FIFRA 24(c).). EPA SLN No. SC-100003. 1 pp.

SePRO Corporation. 2010c. Natrix™ – Special Local Need (SLN) Label (FIFRA 24(c).). EPA SLN No. TX-100010. 1 pp.

SePRO Corporation. 2011a. Natrix™ – Special Local Need (SLN) Label (FIFRA 24(c).). EPA SLN No. ID-110007a. 1 pp.

SePRO Corporation. 2011b. Natrix™ – Special Local Need (SLN) Label (FIFRA 24(c).). EPA SLN No. GA-110006. 1 pp.

SePRO Corporation. 2012. Natrix™ Material Safety Data Sheet. Carmel, IN. 9 pp.

SePRO Corporation. 2014. Natrix™ Aquatic Pesticide. Carmel, IN. 1 pp.

MacroTech® Copper Ion Generator

For over 40 years, ship cooling systems have been protected against macrofouling by the electrolytic dissolution of aluminum and copper anodes. The copper ion generator reduces the settlement of zebra mussel veligers during the summer. Settled veligers are exfoliated in the winter as their absorbed copper level approaches toxic levels. The copper ion generator does not control existing adult populations. Although the copper ion generator doesn't eliminate all macrofouling, it does keep zebra mussel infestations at an acceptable level for some facilities (Blume et al. 1994; Babinec 2003; Mackie and Claudi 2010).

Chemical Name and Formulations

- Chemical Name:
    - copper ions (Cu^{++}) and aluminum (Al)
    - aluminum hydroxide ($Al(OH)^3$)

- Source: MacroTech, Inc. (MacroTech, Inc. 2014)
  246 Mamaroneck Rd
  Scarsdale, NY 10583-7242
  914-723-6185

Mode of Action

Incoming water is treated with copper and aluminum by the controlled electrolytic dissolution of anodes of these materials to produce copper ions and aluminum hydroxide. Presence of copper in water inhibits veliger activity and development through direct toxicity. The aluminum hydroxide has a flocculent activity that aids in precipitating veligers, and it forms an anodic, fluid film on surfaces, which acts as an antifouling coating to inhibit biofilm formation and postveliger settlement. This activity also reduces potential for microbiologically induced corrosion.

Application Strategies

Deploy this device to treat incoming water in flow-through or recirculating service water systems.

Timing of Application

Apply on a continuous basis during the reproductive and settling season to prevent settlement at the postveliger stage.

Application Rates and Techniques

The maintained treatment level is ≤ 5 ppb ionic copper.

Maximum Water Concentrations

The MCL for copper in drinking water is 1.3 mg L^{-1} (USEPA 2009).

Use Restrictions

There are no restrictions on the use of treated water immediately following treatment.

Timing of Results

Copper ions have been reported to cause 100 percent mortality in zebra mussels at a concentration of 5 ppm for 24 hours (McMahon and Tsou 1990).

Toxicological Data

Toxicity data for copper oxide to aquatic species is shown as an example in Table 17.

Table 17. Toxicity of Copper Oxide[1] to aquatic species.

Organism	Test	Result
Water Flea (*Daphnia similis*)	48 hr EC_{50}	42 µg L^{-1}
Zebra Danio (*Danio rerio*)	96 hr LC_{50}	75 µg L^{-1}
Snail (*Biomphalaria glabrata*)	48 hr LC_{50}	179 µg L^{-1}

[1] Kiaune and Singhasemanon (2011)

Precautions

- Monitor water hardness and presence of desirable aquatic species in outfall water.
- Exposure to copper can cause skin and gastrointestinal irritation.

Adjuvant/Detoxicant/Deactivant Use

No adjuvant, detoxicant, or deactivant needed.

Antidote Information

Wash contacted areas. Get medical attention if irritation persists.

References

Babinec, J. 2003. Copper ion treatment for zebra mussel mitigation in house service water systems. *PowerPlant Chem*. 5(9):539-547.

Blume, W. J., P. C. Fraleigh, and W. R. Van Cott. 1994. Evaluation of copper ions and aluminum floc for preventing settlement of zebra mussels. *Proceedings of the Fourth International Zebra Mussel Conference, Madison, WI, March 1994*.

Kiaune, L. and N. Singhasemanon. 2011. Pesticidal copper (I) oxide: Environmental fate and aquatic toxicity. In: *Reviews of Environmental Contamination and Toxicology Volume 213*, ed. D.M. Whitacre,1-26. New York, NY: Springer Science+Business Media LLC.

Mackie, G. L. and R. Claudi. 2010. *Monitoring and control of macrofouling mollusks in fresh water systems, second edition*. Boca Raton, FL: CRC Press.

MacroTech, Inc. 2014. MacroTech copper ion generator. http://macrotechinc.com/macrotech.pdf. Accessed May 9, 2014.

McMahon, R. F. and J. L. Tsou. 1990. Impact of European zebra mussel infestation to the electric power industry. In *Proceedings of the American Power Conference, Chicago, IL, April 1990, 988-997*.

USEPA. 2009. The national primary drinking water regulations. http://www.epa.gov/safewater/consumer/pdf/mcl.pdf. Accessed May 30, 2014.

Potassium Compounds

Although nontoxic to fish and other higher organisms, potassium compounds are toxic to native bivalves and therefore not approved for use in once-through systems. Potassium compounds are suitable for contained or closed-loop systems or fire protection systems (Lewis et al. 1997; Mackie and Claudi 2010).

Chemical Name and Formulations

Chemical Names:

- Potassium phosphate, monobasic, KH_2PO_4
- Potassium chloride, KCl
- Potash

Mode of Action

Potassium causes several changes in zebra mussels, including shell gaping, cessation of ciliary beating, and mortality. It is thought to kill adult mussels by destroying the membrane integrity of the gill epithelium, thus eliminating the ability to respire (Fisher et al. 1991; Wildridge et al. 1998).

Application Strategies

Deliver a potassium-rich solution to the water which is to be treated.

Timing of Application

Potassium toxicity is influenced by water temperature. Toxicity is generally higher at higher water temperatures. Lower temperatures may require longer treatment times.

Application Rates and Techniques

Tests of various potassium salts show that adults are killed rapidly. Table 18 summarizes the toxicities of potassium salts to zebra mussels.

Table 18. Toxicity of potassium salts to zebra mussels.

Potassium Salt	LC_{50} in mg L^{-1}	Reference
KCl	150 (48 hr) 138 (24 hr)	Waller et al. 1993 Fisher et al. 1991
KH_2PO_4	92 (24 hr)	Fisher et al. 1991

A concentration of 50 mg L^{-1} K^+ (as KCl) prevents settlement of veligers (Fisher et al. 1993).

Maximum Water Concentrations

Check with state agencies to see if a NPDES permit is required for facility-specific discharge.

Use Restrictions

Restrict concentrations to maintain permitted discharge limits.

Timing of Results

Treatment effects are seen within 24 hours. Maintain treatment for effective control.

Toxicological Data

Toxicity data for potassium salts to aquatic species is shown as an example in Table 19.

Table 19. Toxicity of potassium salts to aquatic species.

Potassium Salt	Organism	Test	Result
KCl[1]	Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	2010 mg L^{-1}
KCl[1]	Snail (*Physa heterostropha*)	96 hr LC_{50}	940 mg L^{-1}
Potash[2]	Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	68 mg L^{-1}
Potash[2]	Bluegill Sunfish (*Lepidomis macrochirus*)	96 hr LC_{50}	230 mg L^{-1}
Potash[2]	Water Flea (*Daphnia magna*)	48 hr EC_{50} hard water	430 mg L^{-1}
Potash[2]	Water Flea (*Daphnia magna*)	48 hr EC_{50} soft water	200 mg L^{-1}

[1] Daum et al. 1977

[2] Armand Products Company 2012

Precautions

- May be irritating to eyes, skin, respiratory and gastrointestinal tracts.
- Can cause permanent eye damage.
- Harmful if swallowed.

Adjuvant/Detoxicant/Deactivant Use

No adjuvant or detoxification is required.

Antidote Information

The following information is from the MSDS (Armand Products Company 2012):

- Eyes: Immediately flush eyes with water for at least 15 minutes. Hold eyelids apart to ensure complete irrigation. Get immediate medical attention.
- Skin or clothing: Immediately remove contaminated clothing and shoes. Flush contaminated area with water. Discard or launder contaminated clothing. If irritation occurs, get medical attention.
- Ingestion: Do not induce vomiting if swallowed. Rinse mouth with water and give water. Do not give anything by mouth to convulsive or unconscious person. Keep airway clear if vomiting occurs. Seek immediate medical attention.
- Inhalation: Immediately remove person to uncontaminated area. If not breathing, give artificial respiration. If breathing is difficult, administer

oxygen. If pulse or respiration stops, have trained personnel administer basic life support. Immediately call for emergency medical services.

- Emergencies: 1-800-733-3665 or CHEMTREC at 1-800-424-9300

References

Armand Products Company. 2012. Liquid Potassium Carbonate Material Safety Data. Princeton, NJ. 7 pp.

Daum, K. A., L. W. Newland, and J. C. Hagen. 1977. Responses of *Corbicula* to potassium. *Proc. First Intl. Corbicula Symp*. Texas Christian University, pp 215-225.

Fisher, S. A., S. W. Fisher, and K. R. Polizotto. 1993. Field tests of the molluscistatic activity of potassium chloride on zebra mussel veligers. Third International Zebra Mussel Conference, Agenda and Abstracts, Toronto, Canada, February 23-26, 1993.

Fisher, S. W., P. Stromberg, K. A. Bruner, and L. D. Boulet. 1991. Molluscicidal activity of potassium to the zebra mussel, *Dreissena polymorpha*: toxicity and mode of action. *Aquat. Toxicol*. 20:219-234.

Lewis, D. P., J. M. Piontkowski, R. W. Straney, J. J. Knowlton, E. F Neuhauser. 1997. Use of potassium for treatment and control of zebra mussel infestation in industrial fire protection water systems. *Fire Technol*. 33(4):356-371.

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Wildridge, P. J., R. G. Werner, F. G. Doherty, and E. F. Neuhauser. 1998. Acute toxicity of potassium to the adult zebra mussel *Dreissena polymorpha*. *Arch. Environ. Contam. Toxicol*. 34:265-270.

5 Biopesticides

Pesticides derived from natural materials such as bacteria, plants, animals and certain minerals are known as biopesticides. Biopesticides control pests via non-toxic mechanisms and are typically less toxic than conventional pesticides. Generally, biopesticides only affect the target pest and closely related organisms, can be effective in small quantities, and decompose quickly. Biopesticides are registered by the USEPA (USEPA 2014).

ZEQUANOX®

In the early 1990s, the need for new and alternative zebra mussel control options led to extensive laboratory screening of bacteria as potential biological control agents. The CL145A strain of *Pseudomonas fluorescens* was found to be lethal to zebra mussels as well as quagga mussels. In nature, *Pseudomonas fluorescens* is a harmless bacterium that protects plant roots from disease and is found in all North American waterbodies. This bacterium is now formulated as Zequanox®, which was registered by the USEPA in July of 2011. It is composed of dead *Pseudomonas fluorescens* cells that contain natural compounds toxic to mussels when digested. Mussels readily consume Zequanox® as it is perceived as a nonthreatening food source. Zequanox® controls all life stages of zebra and quagga mussels and can be used in semi-enclosed, enclosed, or other confined flowing or static water infrastructures as well as open water (Marrone Bio Innovations 2012, 2013a, 2014).

Scientific Name and Commercial Formulations

This compound has the following characteristics:

- Scientific name: *Pseudomonas fluorescens* strain CL 145A cells
- Formulation: Zequanox®
    - 50 percent active ingredient
    - Dry powder
- USEPA registration number 84059-15

- Source: Marrone Bio Innovations
  2121 Second St., Suite B-107
  Davis, CA 95618
  1-877-664-4476

Mode of Action

Zebra mussels filter Zequanox® out of the water and process it as a food source. When the product is digested, the active ingredient (*Pseudomonas fluorescens*) causes zebra mussel mortality by disrupting the epithelial cells lining the digestive system.

Application Strategies

Apply Zequanox® as follows:

- Rehabilitation treatment to kill and/or remove adult zebra mussels.
- Settlement maintenance treatment during spawning season to prevent juvenile zebra mussels from settling within the system.
- Veliger (planktonic) life stage treatment during the spawning season to control the floating and swimming zebra mussels in flowing water or a defined static volume.

Timing of Application

Zequanox® efficacy is dependent on zebra mussel metabolism and feeding activity; therefore, site assessments should be conducted to determine appropriate timing of application.

Application Rates and Techniques

Prior to application, Zequanox® is diluted as follows:

In a double contained plastic mixing tank, tote, or similar container appropriate for use in chemical application in aquatic environments, mix 2.2 (1 kg) pounds of dry Zequanox® into 2 to 3.5 gallons (8 to 13 liters) of non-chlorinated water to achieve a slurry concentration of 18 to 10 ounces of Zequanox® per gallon (125 to 77 g Zequanox® per liter) of water or 9 to 5 ounces of active ingredient per gallon (62 to 38 g active ingredient per liter) of water. Mix well and follow application instructions.

Zequanox® is applied as follows in semi-enclosed or enclosed systems (Marrone Bio Innovations 2013a):

- Rehabilitation treatment: In cold water environments one treatment per year is required. In warm water environments, rehabilitation treatments are typically conducted once per year, but cannot be conducted more than twice per year.
    - Flowing water: Using standard chemical injection metering pump inject diluted Zequanox® into flowing water at a point with heavy mixing to reach a homogenous and well mixed suspension of up to 0.027 ounce of active ingredient per gallon of water (200 mg active ingredient per liter). Maintain continuous injection for 6 to 12 hours or until a concentration of up to 0.027 ounces per gallon is reached.
    - Static water: Zequanox® should be held in the contained treatment system for 12 to 18 hours. Use a submersible pump to maintain a completely mixed and dispersed concentration.
- Settlement maintenance treatments: Repeat injection up to two times per month during zebra mussel spawning season.
    - Flowing water: Using standard chemical injection metering pump inject diluted Zequanox® into flowing water at a point with heavy mixing to reach a homogenous and well-mixed suspension of up to 0.0067 ounces of active ingredient per gallon of water (50 mg active ingredient per liter). Maintain continuous injection for 1 to 6 hours until a concentration of up to 0.0067 ounces per gallon is reached.
    - Static water: Zequanox® should be held in the contained treatment system for six hours at 0.0067 ounces of active ingredient per gallon of water (50 mg active ingredient per liter).
- Veliger (planktonic) life stage treatment: Zequanox® is applied at 0.0067 ounces of active ingredient per gallon of water (50 mg active ingredient per liter) applied for up to 12 hours per treatment. Treatments are limited to one per specific volume of water transferred and cannot exceed 0.0067 ounces of active ingredient per gallon of water.

Zequanox® is applied as follows in open water (Marrone Bio Innovations 2014):

- Adult treatments: Apply at a rate no greater than 0.013 ounces of active ingredient per gallon of water (100 mg active ingredient per liter) for up to eight hours. Do not treat more than once per month and no more than four times per year.
- Juvenile treatments: Apply at a rate no greater than 0.0067 ounces of active ingredient per gallon of water (50 mg active ingredient per liter) for up to eight hours. Do not apply more than every two weeks.
- Veliger treatments: Apply at a rate no greater than 0.0067 ounces of active ingredient per gallon of water (50 mg active ingredient per liter) for up to eight hours. Do not apply more than every two weeks.

Treatments to open water can be made via surface or subsurface applications.

Turbidity measurements can be used to determine whether desired concentrations of Zequanox® have been achieved. To correlate target turbidity to desired concentration do the following: in a glass or plastic container, add a known volume of water and the necessary volume of diluted Zequanox® to reach target concentration. Mix and read turbidity. This turbidity reading will be the target turbidity for the desired concentration.

Apply product within one hour of wetting.

Maximum Water Concentrations

See Application rates for maximum use rates.

Limitations on discharge of treated water will be at the determination of the NPDES permitting authority.

Use Restrictions

Do not discharge effluent containing this product into lakes, streams, ponds, estuaries, oceans, or other waters unless in accordance with the requirements of a NPDES permit and the permitting authority has been notified in writing prior to discharge.

Do not discharge effluent containing this product to sewer systems without previously notifying the local sewage treatment plant authority. For guidance, contact your state water board or regional office of the USEPA.

Before applying to open water, notification to the NPDES permitting authority and the local state fish and game agencies is required.

Zequanox® is toxic to bivalves and fish. Do not apply during critical breeding seasons.

Do not use chlorinated water to mix solution.

If mixing with other products, follow the most restrictive label.

Do not apply more than once every two weeks.

Timing of Results

Effects occur over a 3–to-21-day period following application. Efficacy is dependent on zebra mussel metabolism and feeding which is influenced by breeding activity and temperature.

Toxicological Data

Signal Word: Caution

Toxicity data for Zequanox® to aquatic species is shown in Table 20.

Table 20. Toxicity of active product, Zequanox®[1] to aquatic species.

Organism	Test	Result
Rainbow Trout (*Oncorhynchus mykiss*)	96 hr LC_{50}	150 mg L^{-1}
Bluegill Sunfish (*Lepomis macrochirus*)	96 hr LC_{50}	135 mg L^{-1}
Blue Mussel (*Mytilus edulis*)	72 hr LC_{50}	1,612 mg L^{-1}
Freshwater Mussel (*Anodonta sp.*)	72 hr LC_{50}	>500 mg L^{-1}
Water Flea (*Daphnia magna*)	72 hr LC_{50}	255 mg L^{-1}
Freshwater Shrimp (*Hyallela azteca*)	10 day LC_{50}	>100 mg L^{-1}

[1] From MSDS (Marrone Bio Innovations 2013b)

Precautions

- Avoid contact with skin, eyes, and clothing.
- Harmful if swallowed or absorbed through skin.
- Causes moderate eye irritation.
- Applicators and mixers/loaders must wear a dust/mist filtering respirator National Institute for Occupational Safety and Health (NIOSH) standards at least N-95, R-95 or P-95.
- Allergic sensitization can be caused by repeated exposure to high concentrations of microbial proteins.

Adjuvant/Detoxicant/Deactivant Use

Detoxification of Zequanox® is not required before discharging treated water.

Antidote Information

The following information is from the MSDS for Zequanox® (Marrone Bio Innovations 2013b):

- Eyes: Rinse gently and slowly with water for 15 to 20 minutes. If wearing contact lenses, remove then after the first five minutes of rinsing. Call a physician or poison control center.
- Skin or clothing: Remove contaminated clothing and immediately rinse skin with plenty of water for 15 to 20 minutes. Call a physician or poison control center.
- Ingestion: Immediately call a physician or poison control center. Drink several glasses of water but do not induce vomiting unless directed to do so by a physician or poison control center. If the victim is unconscious, do not give anything by mouth.
- Emergencies: 1-800-222-1222

References

Marrone Bio Innovations. 2012. The Zequanox® Story : An in-depth review of the discovery and commercialization of a new, non-chemical alternative for invasive mussel control. http://www.marronebioinnovations.com/lightray/site/wp-content/uploads/2012/09/TheZequanoxStory_0912_web.pdf. Accessed March 26, 2014.

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USEPA. 2014. What are biopesticides? http://www.epa.gov/pesticides/biopesticides/whatarebiopesticides.htm. Accessed April 8, 2014.

Appendix A

Matrix Table: This table can be used to help determine which molluscicide is appropriate for specific infestations.

		Controls adults	Controls or prevents veliger settlement	Requires cleaning prior to application (for badly fouled systems)	Requires detoxification or deactivation prior to discharge	Causes formation of trihalomethanes	Requires specialized equipment	Must be or can be used in combination with chlorination	Degrades to nontoxic compounds or is biodegradable	Cannot be discharged within ¼ mile of potable water intake	Can be applied to surface waters
Chlorination	Hypochlorite Chlorine Gas	X	X		X	X					
	Chlorine Dioxide	X	X		X		X				
Ammonia	Oxamine® 6150	X	X	X	X			X	X		
Bromine	ACTI-BROM® 1338 SPECTRUS® OX1201	X	X		X			X			
Quaternary & Polyquaternary Ammonium Compounds	BULAB® 6002	X	X		X			X			
	BULAB® 6086	X	X		X			X	X	X	
	Clam-Trol CT-2	X	X	X	X					X	
	H-130 Microbiocide	X	X		X					X	
	Slimicide™ C-74	X	X	X							
	VeliGON	X	X								
Aromatic Hydrocarbons	Mexel® 432/0	X	X	X							
Endothall	EVAC™	X	X								
Copper Ions	Natrix™	X	X								X
	MacroTech® Copper Ion Generator		X				X				
Potassium Compounds	Potassium permanganate	X	X								
	Potassium phosphate Potassium chloride Potash	X	X								
Biopesticides	Zequanox®	X	X								X

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13. SUPPLEMENTARY NOTES

14. ABSTRACT

Zebra mussels were introduced in the mid-1980s to the Great Lakes of North America via ballast water exchange. These highly invasive mollusks have made negative impacts upon native aquatic ecosystems and have been a major concern to managers of all types of water delivery systems, including potable water treatment, agriculture, industry, power generation, and fire protection. Since this invasive organism's introduction, a number of chemicals and biopesticides with previously known or newly discovered molluscicidal properties have been used to control it. The goal of any chemical control program is to choose products that will be effective against the target organism, will work rapidly, and have minimal environmental impact. This report is an update of an original version, *Zebra Mussel Chemical Control Guide*, by S. L. Sprecher and K. D. Getsinger, report number ERDC/EL TR-001, published in January 2000, and describes basic guidelines for the use of those compounds currently registered with the United States Environmental Protection Agency (USEPA) for control of zebra mussels. Included in Version 2.0 is a summary of the USEPA registration process, as well as up-to-date information on available molluscicide products, their use strategies, formulations, mode of action, application rates and techniques, maximum water concentrations, use restrictions, toxicological data, and precautions on product handling.

15. SUBJECT TERMS

Aquatic Nuisance Species Research Program (ANSRP)
Biopesticides
Invasive mollusks
Molluscicide
Zebra mussels

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